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JOURNAL

OF THE

AMERICAN CERAMIC SOCIETY

A monthly journal devoted to the arts and sciences related to the silicate industries.

Vol. 1

January, 1918

No. 1

EDITORIALS.

TO THE PUBLIC:

The American Ceramic Society announces the publication of the JOURNAL OF THE AMERICAN CERAMIC SOCIETY, the official organ of the Society.

The American Ceramic Society was founded in 1899, for the avowed purpose of "promoting the arts and sciences connected with Ceramics, by means of meetings, for the reading and discussion of professional papers, and by the publication of professional literature."

Up to this time, the publication of this Society has taken the form of a volume of Transactions containing the papers presented at the annual meeting.

At the annual meeting in February, 1918, the Society, realizing the need for a greater activity in the field of Ceramics, authorized the publication of a monthly journal to be devoted "to the Arts and Sciences related to the Silicate Industries." THIS JOURNAL, by reason of the high standards of the American Ceramic Society and because of the advances which this country is making in all that pertains to Ceramics, may well be expected to take first place in the world's contributions to the science and technology of the industries to which it is devoted.

It is to be hoped that it may find a place in every public and institutional library of this country, as additional service to the reading public in general, and to technical men in particular.

COMMITTEE ON PUBLICATIONS.

THE FUEL CURTAILMENT ORDERS.

The Ceramic industry and especially the building materials branch has been vitally interested in the curtailment orders issued by the U. S. Fuel Administration on April 23rd. The orders were the direct result of the fuel shortage of last winter when, in some sections of the country, plants vitally necessary to the conduct of the war were closed down partially or completely for months, on account of lack of coal.

It was quite natural that the building material industry should be selected as the first to be curtailed, as the entire industry consumes approximately 32,000,000 tons of fuel annually, the clay-working branch consuming about one-third of this amount, or 10,000,000 tons. The industry being ranked as a "peace-time essential," and not a "war essential," offered a better opportunity for a larger diversion of fuel than any other industry. Furthermore, as it was found that for every ton of fuel consumed, this industry puts into transportation channels approximately three tons of raw and finished products, a total of 90,000,000 tons, a curtailment in production would result in considerable relief to the badly overtaxed transportation system.

It was never the intention of the Conservation Division of the U. S. Fuel Administration to curtail all non-war industries or to curtail any industry to a point where the demand could not be taken care of by the industry at large. Every effort was made to correctly estimate the demand on each industry for the year 1918 and the percentages used in the orders represent the estimated minimum, not the maximum. One of the principal aims of the orders was to prevent the use of fuel in producing material that would not be used this year, in other words, in producing stock. It is a well-known fact that a manufacturing concern "can do anything but shut down," but under the present conditions, it was out of the question to allow a single ton of fuel to be used unless it was absolutely necessary.

A close study of the orders with their "exception clauses" will show how easy it is for any manufacturer to get a permit to produce more than the minimum, provided, of course, he can show that he has orders for the material, and provided, also, that there is more than sufficient fuel in his district to take care

of the domestic demands and the war industries. These clauses were put into the orders especially for the benefit of those industries in the "red flag" districts, which were working on government orders, and of the plants in the western and southern sections which were not affected by a fuel shortage. Outside of the triangle bounded by lines drawn from Pittsburgh to Boston and from Pittsburgh to Baltimore, known in the Fuel Administration as the "Red Flag District," it is hardly expected that any plant will be refused a permit to produce beyond the minimum specified in the orders, provided they have legitimate orders which are acted upon favorably by the War Industries Board.

Some criticism has been heard from members of the affected industries because very few other industries have been curtailed. There are a great number of good reasons for this. Many industries not curtailed specifically, have been denied fuel by the Federal Fuel Distributors, others have been under almost continuous embargoes issued by the Director General of Railroads, still others, and there are many of these, have been denied raw materials by the War Industries Board.

The cement industry may be taken as an illustration. No curtailment order has been issued to date covering this industry, for the reason that the cement output of the country has been at below fifty per cent. of normal during the first five months of this year. This was entirely due to the plants in the eastern half of the country being denied fuel. In many cases a whole industry uses such a small amount of fuel that a curtailment order would produce negative results, so far as fuel diversion is concerned.

The latest move of the Fuel Administration has been to organize an "Industrial Furnace Section." As the Ceramic industry is the largest user of fuel coming under this heading, with the exception of the steel and coke industries, a great amount of effort will be devoted to it by this new section. Knowing that there is much unnecessary waste in the use of fuel for manufacturing purposes, the section will attempt to conserve fuel through cutting this waste down to a minimum.

Those connected with the various industries can be of great

assistance to the government by starting at once to look over the plants with which they are connected and locating any possible leak. Uninsulated steam pipes, badly cracked kilns, poor burning practice, steam leaks and poorly aligned shafting should be especially looked after.

The section will appoint a force of field inspectors who will inspect each plant and advise with the management. Reports will be made to the Chief of Section with recommendations for changes that will produce further economy. An educational campaign will also be carried on through bulletins and the trade magazines. Every effort will be made to bring about the desired results without using the power conferred upon the Fuel Administration by the Lever Act.

It is naturally expected that the technical men connected with the industries, and especially those associated with the American Ceramic Society will grasp the splendid opportunity offered to assist the country in this time of stress. Many have devoted a great deal of time, for years past, in an effort to conserve our fuel resources, but it has taken a great war to bring the government to the point where it is willing to back them up and even to use compulsion if necessary, to bring about results. It takes little though to foresee the benefits that will result and permanently remain after the war is over.

THE NATIONAL RESEARCH COUNCIL.

The following Executive Order, defining the duties of the National Research Council, was issued recently by the President:

1. In general, to stimulate research in the mathematical, physical and biological sciences, and in the application of these sciences to engineering, agriculture, medicine and other useful arts, with the object of increasing knowledge, of strengthening the national defense, and of contributing in other ways to the public welfare.
2. To survey the larger possibilities of science, to formulate comprehensive projects of research, and to develop effective means of utilizing the scientific and technical resources of the country for dealing with these projects.
3. To promote cooperation in research, at home and abroad, in order to secure concentration of effort, minimize duplication, and stimulate progress; but in all cooperative undertakings to give encouragement to individual initiative, as fundamentally important to the advancement of science.

4. To serve as a means of bringing American and foreign investigators into active coöperation with the scientific and technical services of the War and Navy Departments and with those of the civil branches of the Government.

5. To direct the attention of scientific and technical investigators to the present importance of military and industrial problems in connection with the war, and to aid in the solution of these problems by organizing specific researches.

6. To gather and collate scientific and technical information at home and abroad, in coöperation with Governmental and other agencies and to render such information available to duly accredited persons.

Effective prosecution of the Council's work requires the cordial collaboration of the scientific and technical branches of the Government, both military and civil. To this end representatives of the Government, upon the nomination of the National Academy of Sciences, will be designated by the President as members of the Council, as heretofore, and the heads of the departments immediately concerned will continue to coöperate in every way that may be required.

(Signed) WOODROW WILSON.

THE WHITE HOUSE,

May 11, 1918.

The work in ceramics, which is carried out under the auspices of the Research Council is in the hands of three committees: (1) the Committee on the Chemistry of Cements and Related Building Materials, Prevost Hubbard, Chairman, office of Public Roads and Rural Engineering, U. S. Department of Agriculture, Washington, D. C.; (2) the Committee on the Chemistry of Glass, Arthur L. Day, Chairman, Geophysical Laboratory, Washington, D. C.; (3) the Committee on the Chemistry of Ceramics, Edward W. Washburn, Chairman, University of Illinois, Urbana, Ill.

The last-named committee covers all branches of ceramics not covered by the first two committees. In a future issue we expect to present further details concerning the work of these committees.

EDWARD ORTON, JR.

On February 17, 1898, ten men met in the old Monongahela Hotel, Pittsburgh, Pa., to discuss, in an informal fashion, the possibility of organizing a technical ceramic society. This subject had previously been discussed by Professor Edward Orton, Jr., and Mr. S. Geijsbeek and the time seemed ripe for such a venture. Professor Orton was at that time Director of the only Department of Ceramic Engineering in the United States, having been the pioneer in the application of academic instruction to this field of technology. He had already attained leadership in technical ceramics and was at once looked upon as the guiding spirit of the initial meeting and of all subsequent efforts which led to the formal organization of the American Ceramic Society, a year later. The task of organizing a group of men for this purpose was by no means an easy one. The spirit of conservatism, the clinging to cherished trade secrets, and the more or less well-defined doubt as to the value of the technical study of ceramic subjects, had to be overcome and men won over to the cause of advancement. Orton's perseverance and his potent personality attracted seventeen men willing to become charter members of the proposed organization. His accomplishment may not appear to have been difficult of execution, to the younger generation of today, but those who knew the conditions of twenty year ago will appreciate the magnitude of the task. Professor Orton had prepared for the first meeting an interesting program, which increased the enthusiasm of the charter members and caused others to join the Society. The meeting was a complete success and the novelty of the frank discussion of technical matters aroused wide interest.

With all the powers of his vigorous nature, the subject of this sketch threw himself into the work of completing the organization of establishing the rules, and of adopting a policy which has remained as the foundation of our organization to this day. He attracted to the Society the leading spirits of the ceramic world and created a delightful atmosphere of good-fellowship, existing in but few technical societies. He, nevertheless, insisted upon continuous hard work on the part of the membership and, step



Edward Orton Jr.

by step, he led the organization to the position it now occupies in the industrial world.

Professor Orton has served the American Ceramic Society as Secretary for twenty years, giving to this work his whole-hearted devotion and making sacrifices of such magnitude that any expression of our appreciation of his services seems feeble and inadequate. We are so utterly in his debt.

Finally, when his country called her men to arms, Professor Orton obeyed with characteristic promptness and is now serving as Major in the Department of the Quartermaster General.

For a brief biography of our subject, we copy the following paragraph from "Who's Who in America:."

"Professor Edward Orton, Jr., was born in Chester, N. Y., October 8, 1863. His parents were Dr. Edward and Mary (Jennings) Orton. Mining Engineer, Ohio State University, 1884. On October 3, 1888, he married Mary Princess Anderson, of Columbus, Ohio. Chemist and Superintendent of blast furnaces, 1884-8. The first regular manufacturer of 'ferro-silicon,' or high silicon alloy of iron, in the United States, Bessie Furnace, New Straitsville, Ohio, 1887-8. Entered clay industries in 1888 and managed several plants 1888-1893. In 1893 he began an agitation which resulted in establishing in 1894 the first school in the United States for instruction in the technology of the clay, glass, and cement industries, of which he was continuously, to the spring of 1916, the Director, at which time he was elected to Research Professorship in Ceramics. Dean of College of Engineering, Ohio State University 1902-6, and 1910-16. State Geologist of Ohio, 1899-1906. Fellow A. A. A. S. Member of the Society of Promotion of Engineering Education, American Society for Testing Materials, National Brick Manufacturers Association. Wrote: 'Clays of Ohio and Industries Established upon Them,' *Rep. Ohio Geological Survey*, Vol. V, 1884, 'The Clay Working Industries of Ohio,' Vol. VII, 1893. Also numerous technical articles and reports. Home: 788 East Broad St., Columbus, Ohio."

The Society, at the last meeting, voted to show its appreciation of Professor Orton's services during the past twenty years. Realizing that mere words are inadequate, we present here the portrait of him to whom we owe so much.

ORIGINAL PAPERS AND DISCUSSIONS.

KAOLIN IN QUEBEC.

By J. KEELE, Ottawa, Canada.

Kaolins^m or residual clays of any kind are rarely found in the Archean upland which comprises so large a portion of the Provinces of Quebec and Ontario. Although feldspar dikes are frequent in this area, they are mostly fresh and unaltered even at the surface and kaolinization or even semi-kaolinization is seldom evident. For these reasons the isolated deposit of kaolin of workable dimensions which occurs at St. Remi is remarkable, and so far as we know at present, is unique in the Province of Quebec. The property is owned by the Canadian China Clay Company and is situated near the village of St. Remi, Amherst Township, Labelle County, about 70 miles northwest of Montreal. It lies a short distance north of the magnesite deposits described by Wilson.¹

The kaolin occurs in a north and south trending drift covered ridge, about one-half mile in width, which intervenes between higher rocky ridges of granite and syenite gneiss and from which it is separated by well-marked depressions. Wherever the kaolin has been exposed in working and prospecting, the bed-rock that contains it is the Grenville quartzite, in vertical or nearly vertical beds, trending in a northwesterly direction. The main body of kaolin enclosed in the quartzite beds lies along the western slope of the ridge. The quartzite wall rock on the east of the kaolin is mostly massive, but on the west side (Fig. 1) it is shattered and friable for a width of 800 feet. Throughout most of the shattered zone the quartzite is permeated by small stringers or

¹ *Trans. Am. Ceram. Soc.*, 19, 254-259 (1917).

leads of kaolin, varying from a fraction of an inch to four feet in width. The main body of kaolin has been uncovered in one place continuously for about 1400 feet and has been traced, by test pits and trenches, for at least 7,000 feet. The width varies from an extreme of about 100 feet to less than 20 feet. In a boring, kaolin was encountered to a depth of 150 ft. The covering of glacial drift varies from 2 to 10 feet in thickness.



FIG. 1.

Quartzite wall rock in the kaolin mine at St. Remi, Quebec, showing vertical and horizontal lines of fracture. The overburden is glacial drift.

Most of the known occurrences of kaolin are due to alteration of the rock *in situ*, but the deposit at St. Remi appears to have been deposited in its present position in the quartzite from an extraneous source, the silica of the quartzite having been replaced by kaolin. The surfaces at the planes of faulting and fracture of the quartzite rock have been channelled by the solution of the silica, and kaolin now occupies the channels. There are large masses of mixed quartz grains and kaolin, in the main lead, which still show the original structure of the quartzite

rock. The boundaries of the kaolin are irregular, following the zone of greatest fracturing in the quartzite. Where the quartzite is dense and unbroken there is no kaolin. The quartzite contained so little feldspar originally that less than one per cent. of the kaolin could be accounted for from this source.

There are two other sources of kaolin, the one being the orthoclase in the beds of garnet gneiss included in the quartzite, the other, the batholithic masses of granite and syenite which adjoin the quartzite belt, with occasional dikes of the latter. One of the syenite dikes in the quartzite was partially weathered, the chemical composition being similar to that of cornish stone. The kaolin may have been formed by rising igneous waters acting on the feldspars of the surrounding masses and moving freely in the fractured zone of the quartzite, the presence of tourmaline being one of the evidences of pneumatolytic action.

There are several masses of buff and pink kaolin present in the main lead which may owe their discoloration to the percolation of water through the overlying drift. Over a large part of the deposit, however, a snow-white clay is in direct contact with the drift, so that the discoloration may not be all accounted for in this way. Certain of the beds, included in the quartzite, contain iron-bearing minerals, the decomposition of which probably contributed a portion of the stain.

China Clay.—A washing plant, Fig. 2, was erected and placed in operation in 1912 and washed china clay has been produced since that time. Most of the washed product is supplied to the paper trade, although several carloads have been shipped to potteries in the United States. The capacity of the plant has been increased to meet the greater demand for kaolin during the past few years. The crude material, consisting of a mixture of quartz particles and clay, with a small percentage of finely divided tourmaline, yields, upon washing, about 40 per cent. of china clay. This clay is more plastic and has a greater shrinkage than the English china clays. Its softening point is cone 34. The excellent quality of the washed clay is indicated by its chemical composition: Silica 46.13 per cent., alumina 39.45 per cent., total fluxes 1 per cent., the balance being combined water.

The kaolin first mined from the deposit was uniformly white

but as the mining and stripping progressed southward, a large amount of discolored clay was encountered. This discolored clay contains about 2 per cent. of iron oxide and develops a light red color upon burning and is obviously not included with the whiter material in washing. The discolored material being quite refractory, its utilization in the manufacture of second quality fire brick is proposed and a small plant for this purpose will be erected at the mine during the coming winter. Some portions of the discolored clay contain sufficient quartzite to pro-

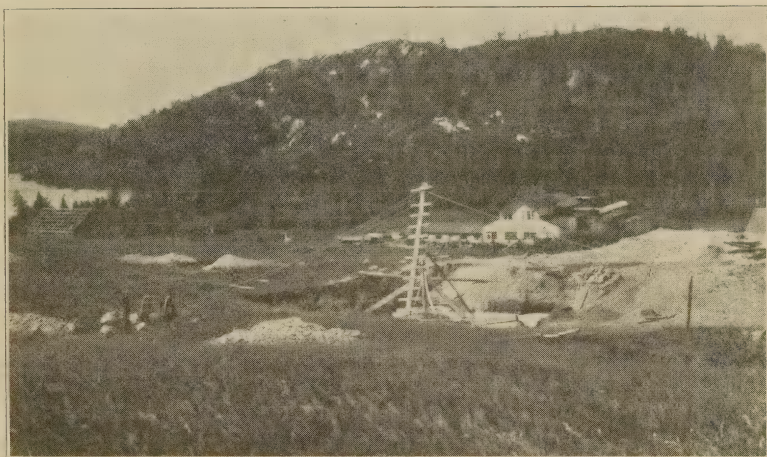


FIG. 2.

Kaolin mine and washing plant of the Canadian China Clay Company at St. Remi, Quebec, in 1912.

vide the necessary grog for brick making, without further additions. Additional amounts of quartzite for this purpose are available in the crumbling west wall. The discolored clay when washed is far more plastic than the white, in fact its working qualities are such that it can be thrown on the potters wheel almost as well as a stoneware clay, and may possibly be utilized in the manufacture of novelty pottery. The discolored clay has the open burning qualities of a kaolin, so that if a dense body, maturing at a low temperature is desired, its mixture with a vitrifying clay is necessary.

Silica Products.—The shattered and friable quartzite occurring along the western flank of the deposit is permeated throughout by specks and stringers of kaolin. A washing test of a sample collected over 150 feet, at right angles to the kaolin vein, showed that 11 per cent. passed a 200-mesh screen and that most of this fine material was kaolin. The character of this rock suggested that it might be used in the manufacture of silica brick of the ganister type, by simply milling the rock in a wet pan and moulding it into brick shapes. The preliminary tests for this purpose indicated that the behavior of the quartzite under heating and the character of the bond produced were excellent. There seems to be no doubt that a clay-bonded silica refractory brick, having a wide range of usefulness, may be produced from this material. The amount of raw material available for this purpose is unlimited.

It is proposed to break down the quartzite in dry pans and to subject the ground product to a washing process which will yield a clean quartzite sand, suitable for the manufacture of glass and carborundum. A laboratory test for this purpose demonstrated that most of the wall rock, when crushed, yields a sand of the proper texture, and having the following analysis: Silica 99.25 per cent., alumina 0.06 per cent., iron oxide 0.69 per cent. If a suitable commercial process can be devised for treating the wall rock, the utilization of that part of the deposit for this purpose is most promising.

COMMUNICATED DISCUSSIONS.

H. RIES: The kaolin deposit of St. Remi, described by Mr. Keele, is probably one of the most interesting in North America. As he states, it is exceptional to find kaolin deposits within the glaciated region, as the advance of the continental glacier scraped off practically all residual clay that had formed in pre-glacial times. It is conceivable, of course, that some residual material might have remained because of the fact that it had accumulated in rather narrow pockets, protected on both sides by hard rock. Deposits of this type have been found at Bedford, Mass., and near Cornwall, Conn. The latter resembles the St. Remi material somewhat in being associated with quartzite.

The question of the origin of the St. Remi material, which Mr. Keele raises, is very interesting, but at the same time it is one that is sometimes difficult to decide. This same question has been agitated for years regarding the Cornwall, England, china clays. Were they formed by weathering, or by the action of vapors or heated waters of volcanic origin rising along fractures in the granite?

I had the opportunity of seeing these St. Remi deposits when they were first opened up, but there was then not as much opportunity for studying them as Mr. Keele has since had.

It seems to me that the association of the clay with fracture zones in the quartzite is not necessarily an indication of its deposition by rising waters, for the fracture planes might also have served as a pathway for descending waters. On the other hand, the apparent absence of feldspar in the fresh quartzite might be against the theory that the kaolin had been formed by the weathering of a feldspathic quartzite.

There is, however, it seems to me a third possibility, *viz.*, that pegmatite solutions have invaded the quartzite in an irregular manner and that the weathering of the pegmatite deposited has yielded the kaolin. Until we get deeper into the deposit, definite proof may be lacking. Indeed there has always been some doubt regarding the possibility of kaolin being formed at depth by rising solutions of magmatic origin, a point which has been discussed somewhat at length by W. Lindgren.¹

R. R. HICE: The occurrence of this deposit is rather unique. The whole region has been so thoroughly glaciated that we naturally expect all products of decay would have disappeared, the time elapsed since the glacial period being too short to give us products of decay in any quantity. I am not personally familiar with this locality, but farther west, where the underlying rock is gneiss, cut by very frequent and often well-developed pegmatite veins, there is no evidence of the weathering of the pegmatite at the surface.

We do know, however, that notwithstanding the intense glaciation which all of this portion of Canada has undergone, in-

¹ "Economic Geology," 10, 89-93 (1915).

cluding the removal of all the products of decay, and generally of all the sedimentary rocks which once covered the gneiss now exposed, there are a few occurrences still remaining of the sedimentary rocks which once covered the gneiss to an unknown distance toward the north. It is therefore clear that occasional spots may be found where all of the products of decay have not been eroded and this occurrence at St. Remi is probably one of these few occurrences.

A hurried perusal of Mr. Keele's paper perhaps raises the question as to whether or not this clay should properly be classed as a kaolin, and again emphasizes the fact that the term "kaolin" has been badly abused by a more or less deliberate misapplication of the term, for the purposes of industrial promotion.

SPECIAL POTS FOR THE MELTING OF OPTICAL GLASS.¹

By A. V. BLEININGER, Pittsburgh, Pa.

It was realized at the very initiation of the work on optical glass, begun in the Pittsburgh Laboratory of the Bureau of Standards about three years ago, that the production of suitable pots plays an important part in the manufacture of this type of glass. It is evident that the pot material must resist corrosion by the glasses, some of which are very active in this respect. The solution of the clay body in the glass causes serious difficulty through the production of striae due to disturbance of the homogeneity, resulting in threads or strings which are stirred into the molten mass. It should be stated here, however, that solution of the pot is not the only cause of striae, but that they may be due to lack of homogeneity in the glass itself. Again, it has been observed that the constituent of the pot body first dissolved by the glass is iron oxide. The coloring power of iron, especially with the heavy flint and barium glasses, is very intense, so that very small quantities suffice to impart to the melt a very decided yellow or green shade. This coloration is injurious not only for optical reasons with reference to photographic purposes, but it is a powerful factor in cutting down the light transmission. Since the use of decolorizers is out of the question in optical glass, owing to the high absorption of light caused by them, it is obvious that the content of iron oxide must be kept down by the use of practically pure reagents and by the use of pots as low in this constituent as possible. It is readily seen that, by the use of the ordinary type of pot, the amount of iron brought into the solution might easily be several times that of the original iron content of the entire glass batch. The use of even the purest reagents would thus be of no avail.

It would appear that pots used for this purpose should be resistant to corrosion by the molten glass, yet sufficiently refrac-

¹ By permission of the Director, Bureau of Standards.

tory to withstand the high temperature of the furnace, which may approach 1475° C, and the hydrostatic pressure of the liquid charge, and should be as low in iron oxide as possible. Since the pots are used but once, the thickness of the bottom and walls may be cut down to the minimum. Owing to the high value of the glass the cost of the pot, within obvious limits, is not a serious consideration.

The first pot mixture used in this laboratory, when operations were begun on a larger scale, was as follows:

	Per cent.
Laclede-Christy bond clay, 69-B.....	6
Tennessee ball clay.....	5
Bond clay from Anna, Ill.....	7
Kentucky ball clay.....	5
"Highlands" fire clay, St. Louis.....	5
N. Carolina or Delaware kaolin.....	12
Calcined "Highlands" clay, 10-mesh.....	20
Calcined kaolin, through 16-mesh.....	40
	<hr/>
	100

In using this mixture it is necessary to calcine the kaolin to a temperature of not less than the softening point of cone 14. This, of course, increased the cost of the pots. Later, the calcined kaolin was replaced by a mixture of 80 per cent. kaolin (N. Carolina, Florida and Georgia in equal parts), 10 per cent. flint, and 10 per cent. of feldspar, fired also to cone 14. This gave a sharper and less friable grog. Both compositions gave excellent results with reference to the standing-up qualities and the resistance of the pots to corrosion. Still, the iron content of the mixture was somewhat too high and it was thought desirable to work out a composition akin to that of a hard porcelain. After some experiments the following composition was arrived at:

	Per cent.
Calcine.....	43
Kaolin.....	25
Plastic bond clays.....	25
Feldspar.....	7
	<hr/>
	100

Here, the calcine consisted of the kaolin, feldspar and flint mixture mentioned above. It is evident that in blending such a number of materials great care is necessary in order to secure thorough dry mixing and pugging. These pots likewise gave very satisfactory results.

The question of procuring the calcine in larger quantities was found to be an annoying one and we cast about for a cheaper source of grog. This was found in the waste bisque of white ware potteries, which is obtainable at a reasonable price and in sufficiently large quantities. This type of body corresponds to the general composition of 35 per cent. kaolin, 15 per cent. ball clay, 14 per cent. feldspar, and 36 per cent. flint. The white granite bisque softens at about cone 30 and possesses, on account of the high flint content, excellent standing-up qualities under conditions of pressure at high temperatures. It is evident that porcelain bisque, whether table ware, electrical porcelain, or floor tile, would not answer for this purpose, owing to the low refractoriness. There would be no objection, of course, to the use of this kind of material in replacing the feldspar introduced, the proportions of white ware bisque and porcelain bisque introduced being such as to maintain the desired refractoriness. In employing white ware bisque, it should be obtained in as clean a condition as possible and care should be taken not to produce too large a percentage of fines (finer than 80 mesh) in grinding. If this grog should become too fine, it might cause serious cracking of the pots during cooling, probably at a temperature of about 625°C when the glass is still in a semi-fluid condition. This defect is due to vitrification, facilitated by the presence of the fine particles of grog and the resulting homogeneous porcelain structure. In satisfactory pots, the grains of grog should still retain their identity as shown by their outlines.

At the present time both white ware bisque and old pot shell (from porcelain type pots) are being used and the composition of the pot batch is as follows:

	Per cent.
White ware bisque, through 10-mesh.....	35
Pot shell, through 10-mesh.....	10
Feldspar.....	3
Flint.....	4
Tennessee ball clay No. 5.....	15
Illinois bond clay.....	5
Kaolin.....	28
	<hr/>
	100

The ground and screened grog and other components of the body batch are weighed, mixed, and then tempered in a wet pan. It is desirable, in tempering, that the mullers be raised about $\frac{1}{4}$ inch off the bottom of the pan so that the grinding action is reduced to the minimum. The clay is then passed through a vertical pug mill and stored as long as possible. The body should be aged at least a month but under our conditions this has not been possible, owing to the demand for pots. The treading of the plastic body has been done away with as unnecessary. The pots are built up by hand in the usual manner and both the open and covered types are made. The pot used in our laboratory is 34 inches in diameter (outside), 27 inches high, and has a bottom 4 inches thick. The wall tapers from $2\frac{1}{2}$ inches (top) to $3\frac{1}{2}$ inches (bottom). The weight of each pot is about 500 pounds. After drying for about four weeks, the pots are ready for the furnace.

One or two pots each week are also being made by the casting process. The composition of this body is as follows:

	Per cent.
White ware bisque.....	48
Plastic bond clay.....	23
Kaolin.....	24
Feldspar.....	5
	<hr/>
	100

The slip used carries 80 per cent. of solids and hence 20 per cent. of water. A mixture of equal parts of sodium silicate and sodium carbonate is used as the electrolyte and the amount added, in terms of the dry weight of the body, is 0.20 per cent.

The arrangement of the mold, as shown in the illustration of Fig. 1, needs no detailed description. It is, of course, necessary to hold the core firmly in position by means of cross beams and tie rods as the upward hydrostatic pressure of the slip is very con-

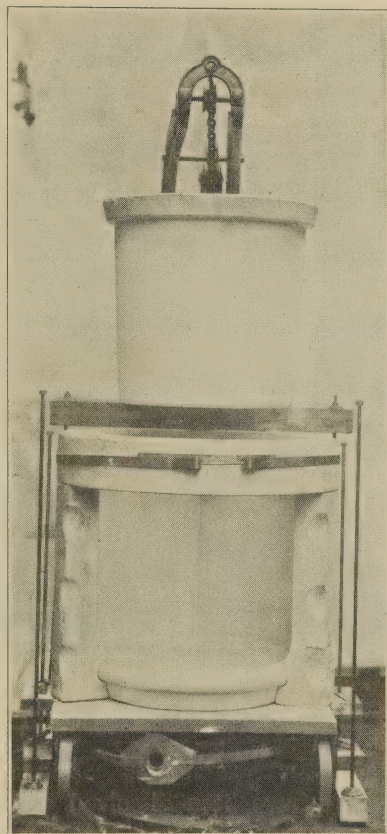


FIG. 1.

Casting mold with core removed.

siderable. The casting, as now practiced, is through three funnels arranged symmetrically around the circumference of the mold. The liquid in the funnels is replenished as the level is lowered. During the last stage of the casting, the settling is

very slow, so that the funnels may be filled and the process allowed to go on without close supervision. Absorption of the liquid ceases after about 16 hours and the core may then be removed. The outer mold may be removed after 24 hours. Suitable hoists are necessary for the handling of the mold parts and the pots.

The process of preparation of the slip is very simple, consisting in introducing the weighed, ground body constituents into a double blunger together with the required amount of water in



FIG. 2.

The first set of porcelain pots made at the Pittsburgh Laboratories, Bureau of Standards.

which the electrolytes have been dissolved. When the desired consistency has been attained, the slip is allowed to run into a large bucket which is conveyed to the mold, hoisted and the slip discharged into the funnels. No difficulty has been experienced in drying the cast pots in less than 3 weeks. They have given very good satisfaction in the glass furnaces and, if anything, are superior to the hand-made ones, especially on account of the fact that they have thinner walls, the thickness

varying from 2 to 3 inches. For this reason less time is required in heating up.

In the use of porcelain type pots it is important to raise the temperature of the furnace to not less than 1400°C before the charge is introduced, in order that the body may become vitrified. The temperature is then lowered and the glass batch is introduced into the pot. Unless this is done, the benefits of the porcelain structure are lost and the pot may corrode as much, or more, than one of the ordinary type.

The same body composition is also used in the casting of the stirring rod parts, which are immersed in the glass during the mixing stage of the melt.

Our experiences with pots for the melting of optical glass have been freely imparted to pot manufacturers and makers of fine glass and, as a result, pots of similar composition are being produced by several firms.

The illustration (Fig. 2) shows the first large porcelain pots made in this laboratory, in the fall of 1917. Small porcelain pots, holding about 30 pounds of glass, were first used by us in May of the same year.

COMMUNICATED DISCUSSIONS.

C. H. KERR: I have been exceedingly interested in reading this paper, my chief thought being one of regret that so few readers have been through the mill so as to have the correct perspective to appreciate the work presented. Nothing, but the actual experience of working on and solving (more or less completely) the problem of making a pot that permits the production of real optical glass, can give one a proper realization of the great difficulties involved. Very few people, even among those who have had some contact with optical matters, realize how absolutely we depend upon optical glass in this great war.

Practically all of the materials used in all industries offer some possibility of substitution. It is frequently difficult, in the use of structural materials, to obtain results by the substitution of materials that are fully equal to the original, but almost always an approximate substitution can be made. This is not true

in the optical glass work. We must have the optical glass for fire control instruments for our Army and Navy and nothing will take its place.

It is very fortunate, although not generally realized by the American people, that we now have an optical glass industry in this country well started and we are able to take care of our military requirements with a very considerable degree of satisfaction. Contrary to usual belief, the production of optical glass is not, at the present time, the limiting feature in the production of optical instruments for fire control purposes.

Throughout the development of the optical glass industry the manufacture of a pot in which it is possible to produce a good grade of optical glass has always been of the first importance and, very frequently, it has been the limiting feature in a particular line of work. For the production of most of the types of optical glass it has been very difficult to secure clays of the requisite purity and composition and which, at the same time, possess the required working properties necessary to the production of full-sized pots satisfactory for use in the usual optical glass procedure. It is not difficult to get the required purity, or the required composition, but to combine therewith the physical properties of the clay or mixture which are necessary, has been exceedingly difficult. Such clays and mixtures, however, have been found and are being used successfully. So far as the question of general composition is concerned, my experience has been somewhat parallel with that cited in the paper and has demonstrated that compositions of the types indicated produce excellent pot batches.

In optical glass pot making it is especially true, as stated in the paper, that an excess of fine material in the grog is a very frequent source of disaster. This trouble is best overcome by a control of the non-plastic part of the mixture to see that it has previously been burned to a sufficiently high temperature, so that, after grinding, the resulting mass is a comparatively coarse material. If the material is too soft it very easily breaks down into a fine powder.

The casting process undoubtedly has a great future, especially in the manufacture of pots of this type. Probably the most

important advantage lies in the fact that a denser structure can be obtained by the casting process. The most important application of this point is in the fact that a mixture of a density such that it is hardly practical for use by the ordinary hand-forming process, can be worked very satisfactorily by the casting process. Along this same line, it is possible to increase the rapidity and safety of the drying process when using cast pots, which has the double advantage of being commercially superior for an ordinary batch and also making commercial a batch which, by the usual process, is hardly capable of commercial handling. Another very great point in favor of the casting is the great increase in homogeneity of the mixture to a degree which is not at all possible by the usual hand-forming method.

E. W. TILLOTSON: Dr. Bleininger has brought out one point that may well be given consideration by all users of glass pots. He states that a pot of the porcelain type, to be efficient, must be burned at a temperature considerably above that of the glass furnace. Such a procedure is rarely or never followed in a glass factory. In fact, the pot arch seldom reaches furnace temperature and the result is incomplete burning, especially of the bottom of the pot.

It would appear that the glass maker should give serious attention to the revision of the construction of the pot arch for the purpose of securing a more even burning of the pot and in order that, by burning at a higher temperature, a pot may acquire its maximum density. Such a procedure may be expected not only to lengthen the life of a pot but also to improve its service as regards corrosion, etc.

C. E. FULTON: Mr. Bleininger has covered the subject very thoroughly and there does not seem to be anything of value which I can add in the form of discussion. We have gone through practically the same experience and while the composition of our optical pot batch is somewhat different from that developed by the Bureau, it is essentially the same type, the chief problem, of course, being to secure a pot with a very dense structure and containing a minimum amount of iron. We contemplate making

some pots following the formula given by Mr. Bleininger, in order to see how they compare with the pots we are now using.

D. W. ROSS: A matter of prime importance in connection with this paper is that glass pots made in accordance with the lines therein laid down are today being used in practically all the optical glass plants of the country and are producing the desired results. Thus, a great burden of experimenting has been cleared away from the optical glass manufacturer and the pot manufacturer alike.

The compositions, as given for both fire clay and semi-porcelain pots, should form a foundation from which other branches of the glass industry may work out pots, etc., suitable for their special needs.

C. R. PEREGRINE: The Society is fortunate in having papers like this by Mr. Bleininger contributed to its Journal.

It would be interesting to know how much corrosion takes place when the pots have been properly preheated, and whether this is greater for the cast pots than for those built up by hand in the usual way.

The policy of the Bureau of Standards, through its Director, which makes its experience available to manufacturers, points toward a new era in which coöperation will do much to place American industries in the front rank.

A. V. BLEININGER: I believe there is nothing to be added to the above discussion. The question of Mr. Peregrine is already answered in the text.

THE EFFECT OF GRAVITATION UPON THE DRYING OF CERAMIC WARE.

BY EDWARD W. WASHBURN, Urbana, Illinois.

That the force of gravitation is able, under certain conditions, to appreciably influence the drying of a mass of clay, was called to the writer's attention as a result of the following experience:

A ball of moist, plastic clay about four inches in diameter was placed on the shelf of an ordinary chemist's desiccator, the lower part of which was filled with water, the idea being to keep the air surrounding the ball of clay moist so that the clay would not dry out on standing overnight. It happened that the clay was left in the desiccator for a month, and at the end of this time it was found to have dried out so completely that it readily broke into pieces when dropped upon the floor. On examination even the central portions of the ball were found to be hard and dry.

At first sight, this behavior seemed rather astonishing, as the ball of clay was standing in an air-tight vessel only three inches above the surface of the water and the air surrounding the clay should, it would seem, have been almost saturated with moisture. In seeking the explanation for this behavior the writer came to the conclusion that the water had been actually drawn out of the clay mass by the attraction of the earth. In other words, the clay must have dried for the same reason that water runs down hill.

In order to test the conclusion that the force of gravitation was responsible for the drying, the experiment was repeated under conditions of more exact control. For this purpose a 10-gram mass of moist clay (containing 30 per cent. of water) was suspended by means of a wire from the bottom of the rubber stopper of a bottle containing a small quantity of water, the height of the clay above the surface of the water being about 6 centimeters. (See Fig. 1a.) The bottle and its contents were

then completely immersed in a large body of water so as to insure constant and uniform temperature conditions on all sides of the bottle. From time to time the mass of clay was removed from the bottle and weighed. The experiment was continued for eleven days, during which time the mass of clay continuously lost weight at the rate of about 30 milligrams per day. At the end of the eleventh day the mass of clay had lost a total of 0.304

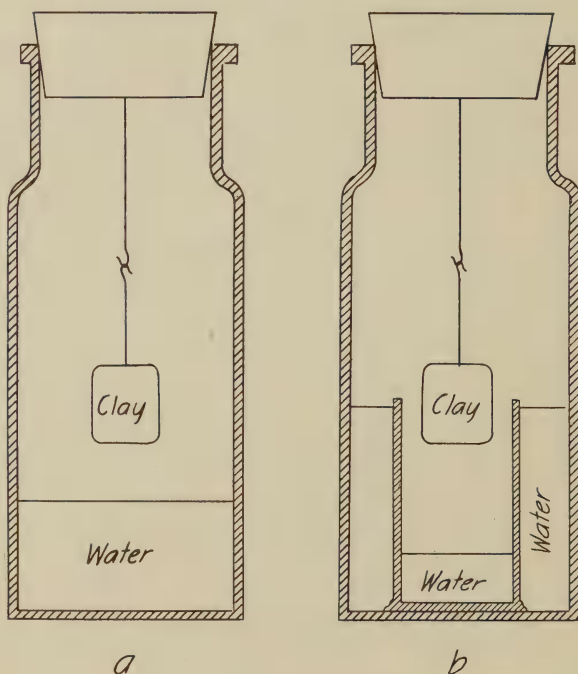


FIG. 1.

gram of water. This water must obviously have distilled out of the clay, under the influence of the attraction of the earth, and condensed into the water in the lower part of the bottle.

To make certain that this was the correct explanation, the mass of clay at the end of the eleventh day was lowered so as to be on the same level as the water in the bottom part of the bottle, but without touching this water, the arrangement being

that shown in Fig. 1b. The experiment was then continued and the mass of clay was found to continuously increase in weight, showing that water was now distilling from the liquid water in the bottle, and condensing into the mass of clay. The distillation in this case was, of course, due to the fact that, owing to the presence of small quantities of soluble materials in the clay, the vapor pressure of the water in the clay was lower than that of pure water. The experiment was carried out in duplicate and the two curves showing the variation of the mass of the clay

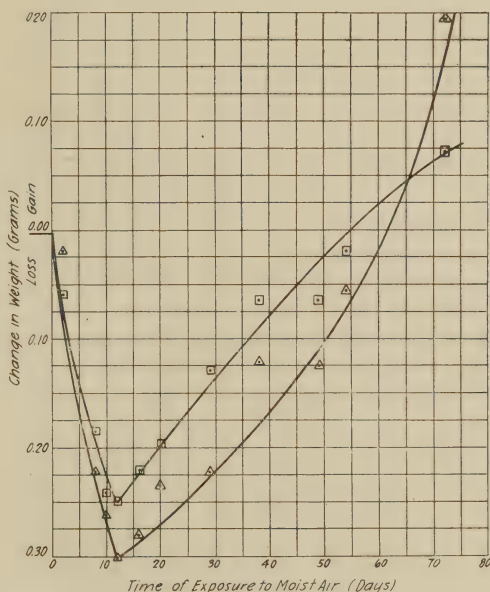


FIG. 2.

from day to day are given in Fig. 2. A repetition of the experiment using a small glass capsule filled with water, in place of the clay cylinder, yielded a similar result.

The only unexpected feature of this experiment was the comparatively great rate at which the water was removed from the clay, under these conditions. Other things being equal, we should expect this rate to be determined by the difference between the vapor pressure of the water in the clay and the partial vapor

pressure of water in the surrounding air. This latter pressure is greatest, of course, at the surface of the liquid water in the bottom of the bottle and decreases steadily with the distance above this surface. The relationship between this latter pressure and the height above the surface of the water is expressed by the equation

$$-dp = gDdh \quad (1)$$

or for short distances, with sufficient accuracy, by the equation

$$\Delta p = gDh, \quad (2)$$

where Δp is the difference in the partial pressure of the water at the surface of the liquid water and at the height h above this surface, D is the density of saturated water vapor at the temperature in question and g is the acceleration due to gravity. For a temperature of 20°C and a height of 6 centimeters we find upon calculation that

$\Delta p = 980 \times 17 \times 10^{-6} \times 6 = 0.1 \text{ bar.} = \text{about } 0.000003 \text{ inch}$
of mercury, which is obviously a very small pressure difference.

Aside from the purely theoretical interest which attaches to the above experiment and conclusion, it is perhaps worth while to point out that in order to keep a mass of moist clay from drying, by inclosing it in a chamber containing water, the water should not be placed at a lower level than the mass of clay which is to be kept moist. Moreover, there would appear to be no reason why the force of gravitation should not be made use of in some cases to control the extent and rate of drying of ceramic ware since, at a given temperature, both of these factors are determined by the perpendicular distance between the piece of ware and the bottom of the containing chamber, provided that the air in the chamber is not stirred. Stirring the air would obviously retard the rate of gravity drying but would of course not stop it entirely unless the stirring were 100 per cent. efficient.

It is also interesting to note that since according to Equation 2 the value of p is proportional to D , the density of the saturated vapor, it follows that the rate of gravity drying would increase with the temperature. That is, a mass of moist clay placed in a gravity dryer filled with saturated steam at 100°C would dry

more rapidly than in the same dryer at 0°C , although at the latter temperature the air in the dryer would contain very little moisture. In other words, the rate of drying in a gravity dryer is determined by the vapor-pressure *gradient* in the dryer and not by the dryness of the air in the dryer. Indeed, as we have seen, the more moisture the air of such a dryer contains, the more rapid will the drying be, a conclusion which at first sight appears paradoxical.

In this connection attention may also be called to the fact that, in operating a moist closet for storing prepared clay, the drying action of gravity upon this clay cannot be eliminated by hanging wet cloths along the sides of the closet, provided the action of capillarity is depended upon to keep these cloths wet; that is, provided they are supposed to be kept moist by having the lower ends dipping into water in the bottom of the closet. It is true that in such a manner the water placed in the lower part of such a closet may be lifted to the same level as the clay, but such water (*i. e.*, water held up by capillary force acting against gravity) will be under tension and the effect of tension upon a liquid is always to lower its vapor pressure. In fact the vapor pressure at the surface of the meniscus in a capillary tube (in which equilibrium has been established between gravity and surface tension) will be identical with the vapor pressure at the surface of the water outside of the capillary tube, although this latter surface will be at a lower level than the surface inside the capillary. This statement will be true regardless of the size of the capillary; that is, regardless of how great the difference in the two levels inside and outside may be.

Although not bearing directly upon the subject of this paper, it is perhaps worth while pointing out in this connection that a method for the direct measurement of the osmotic pressure of any very dilute solution may be based upon Equation 1. The method requires no membrane of any kind and consists simply in finding, by experiment, at what height above the surface of the pure solvent a small quantity of the solution must be placed in order that it shall neither gain nor lose weight by gravity distillation. This height is identical with the height of the osmotic

column, as can be readily demonstrated by purely thermodynamic reasoning. The method would, of course, in practice, be restricted to solutions of such dilution that the height of the osmotic column would not be inconveniently great. It seems quite within the bounds of possibility that an accurate technique could be worked out for applying this method, which would have many obvious advantages over the other colligative property methods in the case of very dilute solutions.

In addition to the cases discussed above it seems probable that the influence of gravity upon vapor pressure also plays an important part in some of the phenomena connected with the swelling of colloidal gels. Thus it has been observed¹ that if a gel, which has been soaked in water until the swelling has reached its maximum, be then raised out of the water, the gel loses most of its water and consequently shrinks greatly in volume. The water lost in this way must evidently have distilled out of the gel under the influence of some force acting upon the water in the pores of the gel but not upon the liquid water below it. In view of the experiments recorded in this paper, it seems highly probable that the force of gravitation is responsible for this behavior. It is also probable that some experimental results obtained by Foote² are likewise the result of the influence of gravitation.

DISCUSSION.

PROF. WATTS: I would like to ask Dr. Washburn if the two clays were the same or different clays.

DR. WASHBURN: The same clay.

PROF. WATTS: Have experiments been conducted to show the difference in the rates at which very dense or open clays

¹ Schroeder, *Proc. Amsterdam Acad.*, **15**, 1078 (1913); **17**, 92 (1914). The so-called Schroeder's paradox was further studied by Wolff and Buchner (*Z. physik. Chem.*, **89**, 271 (1912)) who found, when precautions were taken to conduct the experiment so that gravitation could not act differently upon the water and upon the swollen gel, that under these conditions no difference between the vapor pressures of the two could be detected.

² Foote, *J. Am. Chem. Soc.*, **30**, 1390 (1908).

would dry? Do you consider the rate of drying a matter of the size of grain of the clay?

DR. WASHBURN: You can make the rate anything you like by regulating the height at which you place the clay above the water.

PROF. WATTS: This subject brings to my mind a very interesting point in connection with the potter's wet closet. The cup maker has a room in which he keeps his cups subject to jiggling and prior to turning them, the cups remaining in the closet almost indefinitely. They are placed in the closet as soon as removed from the mold and remain until ready for turning. The closet is an ordinary closed chamber, having a large pail of water at the bottom. It is significant that the cups may remain in the closet for a week or ten days, or even longer, before being turned, and yet they appear to be in satisfactory shape for turning and I do not know of any particular reason why the moisture should remain in those cups, unless there is some circulation of the air in the closet. The cup closets are usually chambers built in the side of a large, open room which is normally warmer near the ceiling than near the floor. We may presume that the increased temperature at the top of the room, outside the chamber, develops a warmer zone inside the chamber and maintains circulation of moist air inside the chamber, keeping the cups moist. A potter, in reading this paper of Dr. Washburn's, would immediately raise this question and I believe that my explanation is correct.

MR. LINBARGER: We have conducted a number of experiments on humidity drying systems and find that, when using as high a relative humidity as 90 per cent. when the air in the dryer was not in motion, we get a loss in weight of the material in the dryer. This loss takes place at a definite rate, for when we place the material on an accurately calibrated balance and take frequent readings from the outside, so as not to disturb the air in the dryer, we are able to measure the rate of evaporation. We note, in this connection, that with all other conditions constant, we have more evaporation when we are using a 90

per cent. relative humidity than when the relative humidity is 65 per cent. We have been at a loss to account for this phenomena, but I think Dr. Washburn's paper presents a very satisfactory explanation.

MR. RIDDLE: I would like to ask Prof. Watts if the same conditions are noted in case the walls and shelves of the drying closets are covered with plaster which is kept in a moistened condition? Would the use of plaster materially alter the moisture conditions in the closet?

PROF. WATTS: I was referring to the ordinary wooden construction for the closets. I was not referring to closets having plaster coated walls or shelves.

MR. RIDDLE: I would like to ask Dr. Washburn: under high humidity conditions, is any of the drying due to capillary action? For example, in a tunnel dryer for brick, if the humidity is decreased too rapidly, the flow of moisture from the inside to the outside of the ware is broken.

DR. WASHBURN: In the dryer I speak of, the drying is all due to gravity. The water in the clay gets to the outside by capillary forces to a great extent, but the drying itself is due to gravity. Mr. Watts did not state that the cups did not dry, that is they were not weighed. This action, of course, is a comparatively small one and I think if those cups were weighed, they would have been found to have actually lost water; they might not have lost enough but that they could be turned satisfactorily but they actually would lose water if the air were not stirred.

MR. BARRINGER: I think this paper touches upon fundamental questions in connection with drying, and in discussing them we should be very careful not to lose sight of the proper relation of the various factors affecting drying. One of the gentlemen spoke of "humidity bringing about quick drying or the loss of moisture." Undoubtedly, the high humidity was applied with a certain temperature, and it is practically impossible in drying to separate the various elements concerned.

As I understand it, the theory of drying involves controlling the relation of the vapor pressure of the water in the ware and the pressure of the vapor of the air, outside the ware. There are factors affecting both of these. For instance, the vapor pressure of the water in the ware increases as the temperature, and the pressure of the vapor outside (the moist air) increases as the humidity. The first step in drying is to balance these pressures. There is another factor that must be considered in drying, and that is, the heat conductivity of the clay wares themselves. Very often when we speak of high temperature, we do not mean the temperature of the clay ware itself, but the temperature of the air.

It seems to me that this element of the mechanical motion of the water ought to be considered in connection with the theory of drying and the fundamental considerations I have mentioned. I would like to ask Dr. Washburn whether, under this drying by gravity, he would classify centrifugal force? Suppose you should rotate a piece very rapidly; would the water not tend to leave the clay upon the same principle as by gravity?

DR. WASHBURN: The rotation would tend to increase the pressure of the water on the periphery; an increase of pressure on a liquid always increases the vapor pressure of that liquid.

MR. DAVENPORT: I would like to ask Dr. Washburn if he had an increasing concentration of moisture in the lower portion of the sample?

DR. WASHBURN: No, the sample was very small, I did not attempt to detect it, but of course the upper part must have dried faster than the lower part.

PROF. WATTS: I would like to ask Dr. Washburn if the mechanical operation of removing this piece from the atmosphere in the bottle, and weighing, could have had any material effect as regards the evaporation of the moisture that might have been carried to the surface of the piece?

DR. WASHBURN: In answer to Mr. Watts' question, I will say no, not as far as the correctness of the final result is concerned;

the effects he mentions would merely produce slight irregularities in the points along the curves, but when the clay was lowered to the surface of the water and began to increase in weight, it showed that the effect you mentioned could not have vitiated the conclusions in any way.

TEST OF A PRODUCER GAS-FIRED PERIODIC KILN.¹

By C. B. HARROP, Columbus, Ohio.

I. Introduction.

The use of producer gas in connection with continuous ceramic kilns has undoubtedly passed through the purely experimental stage. Suggestions that producer gas be used in individual periodic kilns was at first looked upon with considerable suspicion and doubt and some of our recognized engineers even stated freely that the plan was not practical, offering as their reason the belief that producer gas, being a comparatively lean gas and low in calorific value, could not be used for high temperature work, except that hot air be used to support combustion.

One of the first practical attempts to use producer gas, in connection with periodic kilns, was made at the plant of the U. S. Brick Company, at Tell City, Indiana, where a system was installed in 1914. This plant is operating continuously and from a commercial standpoint, the installation has proven entirely satisfactory to the owners. Other plants have since been put into operation, not always successful in every particular, but at least proving that with suitable coal, properly selected and installed equipment and intelligent management, the plan is practical for wares requiring temperatures of 1150° C or lower. To how much higher temperatures it would be practicable to go, tests made so far throw no definite light.

II. The Installation.

(a) **Producer.**—The producer is of the round, stationary pressure type, with a double system of blast piping, delivering steam and air to the bosh as well as to the center tuyère (Fig. 1). The inside diameter of the producer is 10' 6" and it has a maximum gasification rate of 1250 lbs. of coal per hour. The steam is supplied by the main boiler plant of the factory and is carried at 25 lbs. (gage pressure) at the blower.

¹ By permission of the Director, Bureau of Standards.

(b) **Fuel.**—The fuel used was an Indiana coal known as “Washed No. 3 Ayrshire Nut” and was charged at intervals averaging 25 minutes throughout the test.

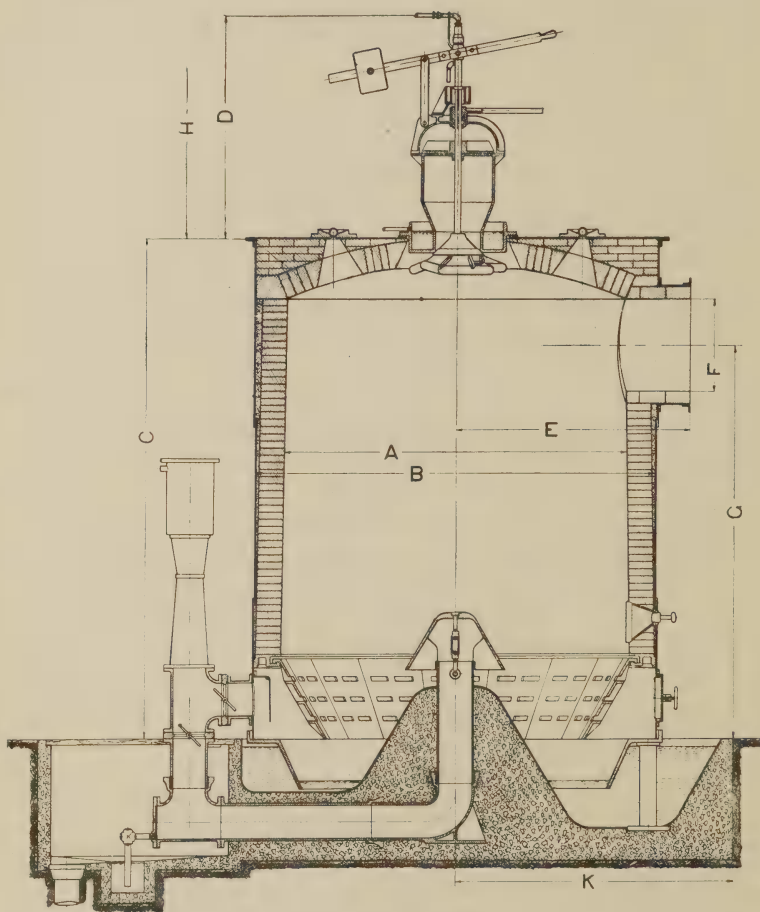


FIG. 1.—Gas Producer.

Each charge of coal was sampled and two combined samples were retained for examination, one covering each half of the period of the test. The two analyses were averaged on the basis of the relative amounts of coal charged during the two halves,

these amounts being indicated in Fig. 2, together with the heating values. The average ultimate analysis was as follows:

Hydrogen.....	6.10
Carbon.....	66.31
Nitrogen.....	1.52
Oxygen.....	20.59
Sulphur.....	0.90
Ash.....	4.58

100.00

(c) **Gas Flues.**—The main gas flue leading from the producer toward the kilns is of brick, with arched top. Its original size was 5' wide by 5' high, but it was found that at the place where

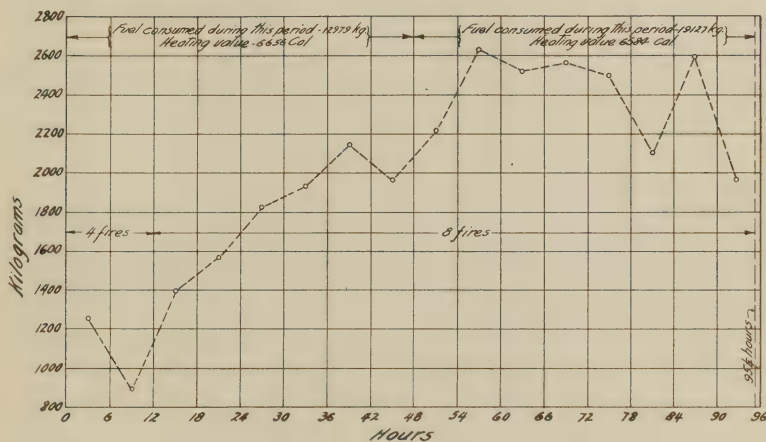


FIG. 2.—Fuel charged into producer over 6-hour periods.

the gas samples were taken, the flue was only 4' deep, evidently due to a deposit of tar and soot in the bottom. There is a thin layer of sand and about 12" of earth fill on top of this main flue.

Two branch flues, 24" wide by 26" high, partly encircle the kiln under test. The burners are connected with these branch flues by laterals consisting of 10" sewer pipe, as indicated in Fig. 3.

(d) **Air Supply.**—Air for combustion is supplied by a No. 9 top angular discharge centrifugal blower, manufactured by the National Blower Company, of Milwaukee, Wis. This blower is

installed in an isolated building and is belt-driven from a line shaft, which in turn, is driven from a 7" \times 12" slide valve throttling engine. The speed of the blower was 845 r. p. m. at the beginning of the test and was finally increased to 1065 r. p. m.

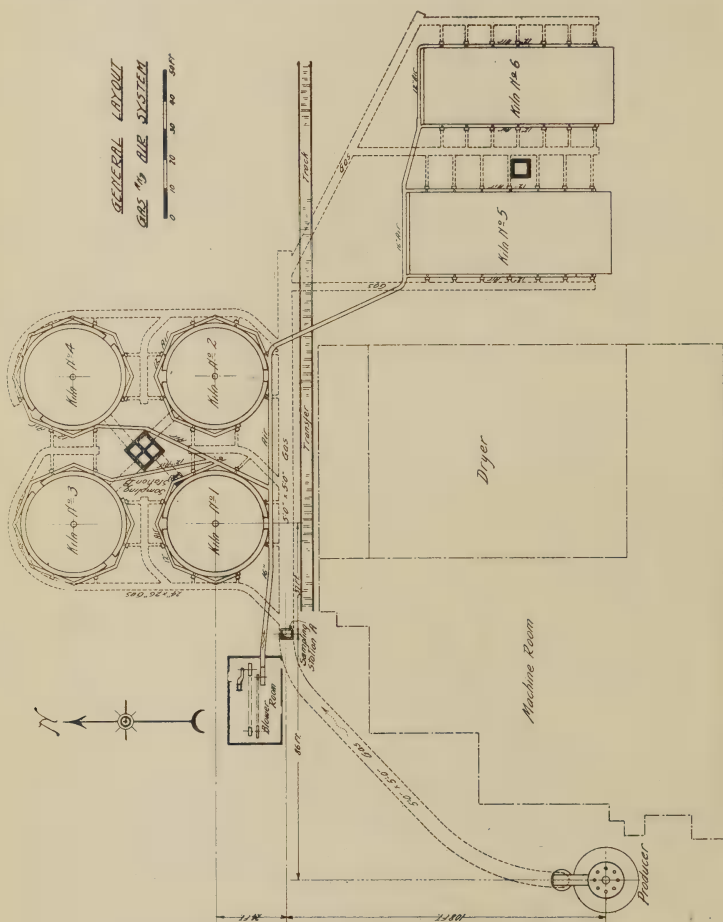


FIG. 3.—Plan of Plant.

(e) **Air Ducts.**—The air blower discharges into an overhead metal pipe of No. 22 gauge steel, 16" in diameter. From this pipe a branch or bustle pipe, 12" in diameter, practically encircles the kiln about on a level with the top of the kiln wall. Con-

necting each burner with this bustle pipe is a 4" diameter down-take fitted with a slide damper.

(f) **Kiln.**—The kiln used for this test, which is of the round down draft type (Fig. 4) and designated as No. 1, is the nearest one to the producer. This was not according to design, but it happened to be the kiln set at the time that the Bureau representatives were free to carry on the test.

This kiln is 30' in diameter, is 7' from the floor to the spring of crown and the crown has a 7' rise. The crown is 12" thick and



FIG. 4.—The kiln.

the side wall 22" thick. The hob is 36" thick and stands about 30" high above the ground. There are eight furnaces provided with rectangular bags, 18" \times 30" inside and 5'3" high. The kiln has two doors, each 4' wide by 5'6" high.

The floor of the kiln is perforated over its entire area and is served by the rather common cross-head-flue draft collecting system.

The main draft flue, the top of which is about 2' below the ground line, is 36" square inside and leads to a 4-compartment chimney, 40' high, situated about 10' from the kiln. Each compartment of the chimney is 36" square and serves but one kiln.

The cast iron burners (Fig. 5) which are of a patented design, are supplied from the underground flues with gas, which passes directly into the central chamber of the burner. For regulating

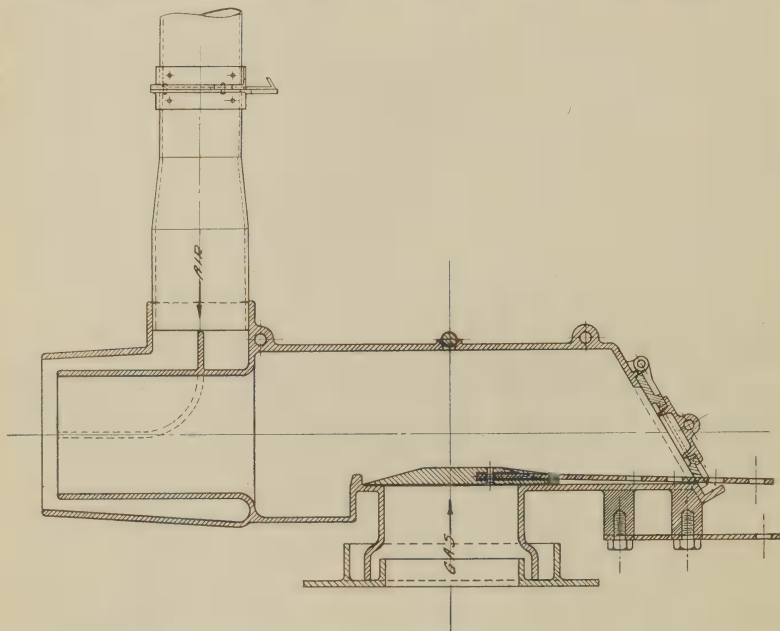


FIG. 5.—Gas Burner.

the gas, there is supplied a flat sliding damper, resting on the bottom of the central chamber, and with a handle for adjusting, which passes through the hinged outer end of the burner. The air for combustion, coming through the downtake, enters an annular space ahead of the gas inlet and surrounding the central chamber, the gas and air not mixing until they leave the inner end of the burner.

The underside of the furnace arch, in the main wall, rises 4"

above the top of the kiln hob, thus leaving an opening 4" high by about 15" long into the furnace chamber.

The kiln is started with four fires only, which continue for the first 12 hours and one full size brick is laid across each of the openings above the hob. At the end of the first 12 hours, the remaining four burners are lighted. In 18 hours after starting two bricks are laid across the openings above the hob and in 30 hours these openings are daubed up tight.

(g) **Ware.**—The product of this plant is common building brick and face brick of the rough or texture variety, the stiff-mud process being employed for both. The raw material is a rather sandy alluvial clay from the immediate vicinity, bordering the Ohio River. This clay, under oxidizing conditions, burns to a deep red color at about cone 02 in the bottom of the kiln. Under reducing conditions, however, the color passes through various shades of tan, brown and finally to gun metal.

Three courses of common (smooth) bricks are set on edge on the bottom and one course on the flat. On top of these are 44 courses of face brick set flat, making a height in the center of the kiln of about 10', unburned. The setting is 3 on 2, in 2-brick benches.

Three and a half to four days is the usual time required to burn one of these kilns. The method followed is to increase the temperature to about 995° C (as indicated by an electric pyrometer, the couple of which hangs through the center of the crown) and then to soak for 24 hours at a slowly increasing temperature. While pyrometric cones are placed in the setting near the wicket, the time of finishing is determined by measuring the settle through the center of the crown. The first settle measurement is taken at about 72 hours and the gas is shut off as soon as the settle totals 11 inches.

III. The Investigation.

(a) **Object.**—Considering the doubt as to the feasibility of this method of burning clay wares that has existed in the minds of many who have been interested in the reduction of kiln burning expense and labor, it was believed that an investigation of the system would show whether or not it embraced any real points of merit.

When compared with results of similar tests made on solid-fuel-fired, natural gas-fired or oil-fired kilns, and taking labor into account, it can be seen wherein and to what amount, one has an advantage over the other.

It was not desired to make a test of the particular producer in use, but as the producer is a part of the system, it was necessary that the investigation include both producer and kiln. In analyzing the results, we can consider the system as a whole, or, we can consider merely the kiln as being supplied with gaseous fuel of a certain composition and at a certain temperature, and study its performance under the existing conditions.

(b) **Apparatus.**—A Hygrodeik was used for determining the temperature and humidity of the atmosphere.

A platform scale was used for weighing the coal charged.

A train, consisting of a water-jacketed glass tube and an asbestos packed glass filter,¹ was used for sampling the tar and soot from the main gas flue. The gas carrying these ingredients was drawn through the train into a water aspirator bottle. The drawing out of the water from this bottle, between two marked levels, indicated the amount of gas drawn through the train. A thermometer was inserted in the aspirator bottle, the readings of which permitted a correction of volume to a basis of the temperature in the gas main.

For determining the water vapor in the producer gas in the main flue, a glass tube $\frac{1}{2}$ " inside diameter by 18" long was used. This tube was filled three-fourths full of calcium chloride and in the remaining space was placed phosphorus pentoxide. Known quantities of gas were drawn through this tube (passing through the calcium chloride first) in the same manner as in sampling the tar and soot.

An iron pipe sampling tube, having small holes at 4" centers, was used for sampling the producer gas over the entire depth of the main. Gas was drawn continuously from this sampler through a bubble bottle by a water aspirator. A 6-lb. glass sample bottle was used for drawing off samples of gas for analysis, just before passing through the bubble bottle.

A Williams apparatus was used for the analysis of the pro-

¹ *Bur. Mines Tech. Paper*, 137, p. 20.

ducer gas. This was equipped for the determination of methane and hydrogen by the explosion method.

An iron-constantan thermocouple was used in the main gas flue for determining the temperature.

Two platinum-platinum-rhodium thermocouples were used to determine kiln temperature. One of these couples was placed in each kiln door, 4' above the floor, and extended 6" into the setting. The doors were closed by double 8" brick casings, with a 2" air space between.

An incline-tube draft gage was used for measuring the static draft in the main draft flue.

A sampling device, similar to that used for the producer gas, was employed for the flue gases.

An Orsat apparatus was used for the analysis of all of the flue gas samples.

An iron-constantan thermocouple, for determining the flue gas temperatures, was inserted in the draft flue beside the sampling tube.

A Leeds and Northrup thermocouple-potentiometer, located at a central station, was used in connection with all thermocouples.

(c) **Procedure.**—Atmospheric temperature and humidity readings were taken every three hours.

Each charge of coal was weighed and a sample placed in a sealed jar. A record of the coal charged during that period was made each 6 hours. The samples of all coal charged during the first half of the test were combined into a single sample and samples covering the second half combined into a second sample. Proximate and ultimate analyses of these samples were made and their heating values determined.

The crown of the main gas flue was uncovered about 3' west of the first branch flue leading to the kiln under test. This point is designated (Fig. 3) as "Sampling Station A" and all temperatures and samples of producer gas were taken at this location.

2500 cc. (cool) producer gas were drawn through the tar and soot train every two hours and the temperature of this cooled gas, so drawn into the aspirator bottle, was recorded.

The same procedure as above was followed in connection with the moisture tube.

Analyses were made of producer gas samples covering periods of 6 hours, equal portions of the sample being drawn into the bottle every two hours. Analyses were made as soon as possible after the samples were completed.

Temperature (potentiometer) readings were taken every 2 hours, covering the producer gas in the main flue; kiln (at both doors), and the flue gases in the main draft flue. Thermometer readings at the cold junctions of all thermocouples were taken at the same time.

The crown of the main draft flue was uncovered just outside of the kiln hob, this point being designated (Fig. 3) as "Sampling Station B," and all temperatures, draft readings and samples of flue gases were taken at this location.

Draft gage readings were taken every two hours (Fig. 6).

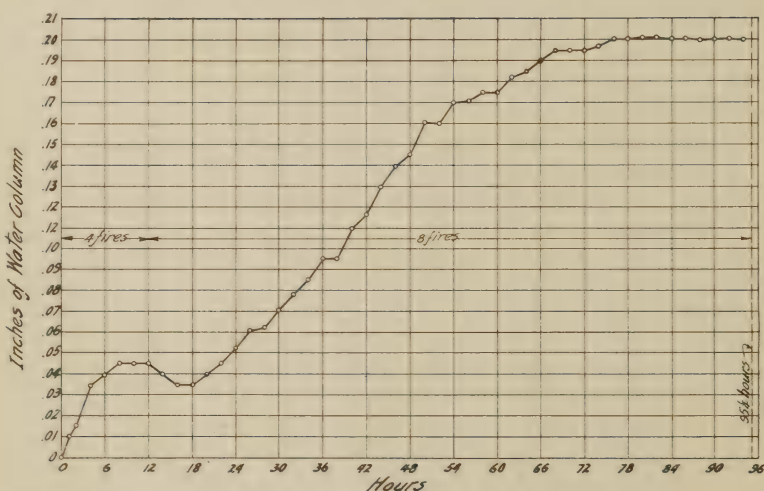


FIG. 6.—Draft in the main draft flue.

Flue gas samples were taken in the same manner as the producer gas samples and the analyses were made as promptly as possible.

Barometric pressure readings were secured from the nearest U. S. Weather Bureau Stations.

IV. The Test.

The handling of the burn was normal in all respects.

The kiln under test was burned for "reds" and contained 9522 smooth brick in the bottom, weighing 5.443 lbs. each, and 62,184 texture brick above, weighing 5.385 lbs. each.

The fires were started at 6 P.M. and burned for $95\frac{1}{4}$ hours. The kiln which was being burned just prior to the test was cut off at 2.30 P.M. and the producer remained idle until 6 P.M. Although instructions were given to maintain the fuel level in the producer until the kiln to be tested was started, this was not done, with the result that the first six hours of the test showed a somewhat greater fuel consumption than would otherwise have been necessary and, of course, this extra fuel was charged against the test. However, this was not a serious matter and does not greatly affect the figures.

The first settle measurement was taken after 71 hours and showed 4". The further progress of the settle is indicated in Fig. 9.

At 62 hours the static pressure of the gas at the burners was 0.14", water gage, and the air pressure, 0.95". At 72 hours the pressure of the gas in the gas main at "Sampling Station A" was 0.12".

CALCULATIONS.

1. Heat from the Coal Fired.—The total amount of coal supplied to the producer during the test was 32,106 kg.

During the first half of the test, 12,979 kg. of coal was used, the average heating value being 6656 Cal. During the last half 19,127 kg. was used, the average heating value being 6584 Cal.

$$12,979 \times 6656 = 86,388,224 \text{ Cal.}$$

$$19,127 \times 6584 = 125,932,168 \text{ "}$$

$$212,320,392 \text{ Cal.} = \text{total heat possible from the coal fired.}$$

2. Volume of Dry Producer Gas.—The proximate analysis of the moisture free ash was

	Per cent.
Volatile matter.....	1.10
Fixed carbon.....	3.08
Ash.....	95.82
	<hr/>
	100.00

As the coal contained 4.58 per cent. ash

$$32,106 \times 0.0458 = 1470 \text{ kg. pure ash in the coal.}$$

$$\text{Then } \frac{1470}{0.9582} = 1533 \text{ kg. ash from the coal supplied.}$$

$$1533 \times 0.0308 = 47.2 \text{ kg. fixed carbon in the ash.}$$

The main draft flue is said to fill up with tar and soot at the rate of 12" in depth per year. The length of the main flue from the producer to "Sampling Station A" was 130 ft. and the width of the flue 5 ft. Therefore, the amount of tar and soot deposited throughout this length of flue during the four day test can be approximated as follows:

$$130 \times 5 \times \frac{4}{365} = 7.12 \text{ cu. ft.}$$

This material had a bulk specific gravity of 1.33.

$$\therefore 7.12 \times 62.4 \times 1.33 = 591 \text{ lbs. or 268 kg. of tar and soot.}$$

As about 93 per cent. of this is carbon, there occurred during the test, a deposition between the producer and the sampling station of 249 kg. of carbon.

As the total coal used was 32,106 kg.

$$32,106 \times 0.6631 = 21,289 \text{ kg. of carbon in the coal fired.}$$

$21,289 - (47 + 249) = 20,993 \text{ kg. of carbon passing the sampling station in gaseous form and suspended in the gas as soot and tar.}$

There was an average of 7.56 g. of tar in each cu. m. of producer gas at the average flue temperature of 580° C. This is equivalent to 23.6 g. of tar in each cu. m. of producer gas at 0° C or 0.526 g. of tar in each gram-molecular volume of producer gas at 0° C. The results of a number of determinations have shown that producer tar contains approximately 90 per cent. carbon.

$\therefore 0.526 \times 0.90 = 0.4724 \text{ g. of carbon per gram-molecular volume of producer gas at 0° C.}$

There was an average of 3.47 g. of soot in each cu. m. of producer gas at the average flue temperature of 580°C . This is equivalent to 10.85 g. of soot in each cu. m. of producer gas at 0°C , or 0.242 g. of soot in each gram-molecular volume at 0°C .

The total carbon from tar and soot per gram-molecular volume of producer gas at 0°C was $0.4724 + 0.242 = 0.7144$ g.

The average of the analyses of the producer gas² samples shows:

7.12 per cent.....	CO_2
21.85 per cent.....	CO
3.25 per cent.....	CH_4

32.22 per cent. carbon-bearing gases.

TABLE I.—ANALYSES OF PRODUCER GAS.

Sample.....	A.	B.	B. ¹	C.	D.	E.	
CO_2	10.31	10.51	8.94	8.70	7.50	7.30	
O_2	0.80	0.60	2.15	0.30	1.60	0.30	
CO	14.43	13.71	15.69	19.60	17.40	19.20	
CH_4	10.41	7.51	2.73	5.23	4.90	6.83	
H_2	8.93	12.36	15.38	12.70	11.41	10.44	
N_2	55.12	55.31	55.11	53.47	57.19	55.93	
Sample.....	F.	G.	H.	I.	J.	J. ¹	K.
CO_2	6.90	7.60	7.60	7.00	8.00	7.78	6.90
O_2	0.20	0.60	0.30	0.50	0.30	0.00	0.20
CO	24.30	20.10	18.30	21.50	18.50	20.01	19.70
CH_4	8.70	8.60	8.36	5.21	6.83	4.24	8.30
H_2	7.18	8.93	7.53	11.98	10.09	13.42	8.79
N_2	52.72	54.17	57.91	53.81	56.28	54.55	56.11
Sample.....	L.	M.	N.	O.	O. ¹	P.	
CO_2	6.90	7.00	7.10	7.20	7.04	7.70	
O_2	0.90	0.10	0.00	0.20	0.23	0.20	
CO	20.10	19.40	17.80	16.90	21.50	20.60	
CH_4	8.17	8.33	8.64	9.85	3.32	7.15	
H_2	8.65	9.48	9.01	6.53	13.16	8.33	
N_2	55.28	55.69	57.45	59.29	54.75	56.02	

¹ Check analyses by the U. S. Bureau of Mines.

² Table I shows the analyses of the producer gas made at the time of the test. Three of these samples were sent to the Bureau of Mines Laboratories for exact analyses and these also are shown. As stated before, the field

$0.3222 \times 12 = 3.8664$ g. = weight of carbon in the carbon-bearing gases in one gram-molecular volume.

$3.8664 + 0.7144 = 4.5808$ g. total carbon in the producer gas per gram-molecular volume.

Then $\frac{20,993,000}{4.5808} = 4,582,824$ gram-molecular volumes of dry producer gas,

or $\frac{4,582,824 \times 22.3}{1000} = 102,197$ cu. m. dry producer gas at 0° C,

or $\frac{102,197}{273} = \frac{x}{273 + 580}$.

$x = 319,319$ cu. m. dry producer gas at 580° C, passing "Sampling Station A" during the test.

3. Weight of Dry Producer Gas.—From the average analyses of the producer gas

		Per cent.
CO ₂	$0.0712 \times 44 =$	$3.1328 = 12.41$
O ₂	$0.0092 \times 32 =$	$0.2944 = 1.17$
CO.....	$0.2185 \times 28 =$	$6.1180 = 24.24$
CH ₄	$0.0325 \times 16 =$	$0.5200 = 2.06$
H ₂	$0.1365 \times 2 =$	$0.2730 = 1.08$
N ₂	$0.5321 \times 28 =$	$14.8988 = 59.04$

————— 100.00
25.2370 g. weight of
one gram-molec-
ular volume.

analyses were made with a Williams apparatus, using the explosion method for determining hydrogen and methane. It is acknowledged that this method is not reliable and a comparison of the analyses in this case shows that the Williams apparatus gives high methane and low hydrogen in each instance. Furthermore, this apparatus is not suitable for gases with high CO content and further comparison of the analyses will show that the Williams apparatus failed to indicate the full amount of CO present. In view of these errors, it was decided to adjust the field analyses to correspond to the exact analyses made in the laboratory, in the following manner: The field analyses of the three samples, sent to the Bureau of Mines, were averaged, as were also the analyses of the same samples made in the laboratory. The average of all the field analyses was then adjusted in accordance with the relation between the average of the three analyses made in the field and those made in the laboratory.

$\frac{4,582,824 \times 25.237}{1000} = 115,657 \text{ kg.} = \text{total weight of the dry producer gas.}$

4. Free Hydrogen and Hydrogen in Methane in the Producer Gas.—

$115,657 \times 0.0108 = 1249.1 \text{ kg.} = \text{free hydrogen.}$

$115,657 \times 0.0206 \times \frac{1}{4} = \frac{595.6}{1844.7} \text{ kg.} = \text{hydrogen in methane.}$

$1844.7 \text{ kg.} = \text{total}$

5. Hydrogen in the Water Vapor of the Producer Gas.—There was an average of 7.85 g. of water vapor accompanying each cu. m. of dry producer gas at the average flue temperature of 580°C.
 $\therefore 319,319 \times 0.00785 = 2,506 \text{ kg.}$ of water vapor in the producer gas or $2,506 \times \frac{1}{9} = 278.5 \text{ kg.} = \text{hydrogen in the water vapor of the producer gas.}$

6. Hydrogen in the Water Vapor Entering the Producer with the Air.— $4,582,824 \times 0.5321 = 2,438,521$ gram-molecular volumes of nitrogen in the producer gas at 0°C.

$32,106 \times 0.0152 = 488 \text{ kg.} = \text{nitrogen in the coal fired.}$

$\frac{488,000}{28} = 17,425$ gram-molecular volumes of nitrogen at 0°C

from the coal.

$2,438,521 - 17,425 = 2,421,096$ gram-molecular volumes of nitrogen at 0°C from the air.

$\frac{2,421,096}{0.792} = 3,056,939$ gram-molecular volumes of dry air.

$\frac{3,056,939 \times 22.3}{1,000} = 68,170 \text{ cu. m. of dry air, at } 0^{\circ} \text{C, entering}$

the producer.

$\frac{68,170}{273} = \frac{x}{273 + 24}$

$x = 74,163 \text{ cu. m. dry air at atmospheric temperature } (24^{\circ} \text{C}).$

The vapor pressure of completely saturated atmosphere at 24°C is 22 mm. of mercury.

The average relative humidity during the test was 75.2 per cent. (Fig. 7).

The average partial pressure of the atmosphere, due to the moisture, was $22 \times 0.752 = 16.54$ mm. mercury.

The average barometric pressure during the test was 756 mm. mercury.

$$756 - 16.54 = 739.46 \text{ mm.}$$

$$74,163 \times \frac{756}{739.46} = 75,822 \text{ cu. m. of moist atmosphere at } 24^{\circ} \text{ C.}$$

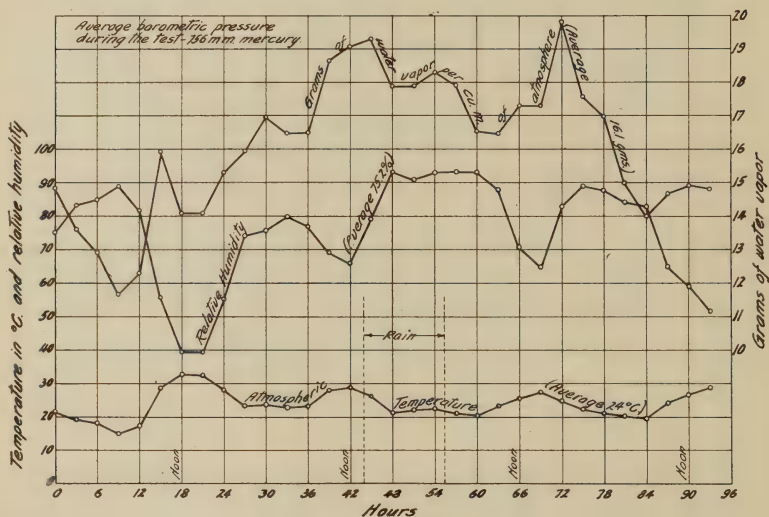


FIG. 7.—Temperature and Humidity of the Atmosphere.

During the test there was present an average of 16.1 g. of water vapor per cu. m. of atmosphere at 24° C.

$$\therefore \frac{75,822 \times 16.1}{1,000} = 1221 \text{ kg. of water vapor entering the producer with the air, or}$$

$$1221 \times \frac{1}{9} = 135.7 \text{ kg. of hydrogen.}$$

7. Hydrogen in the Tar Carried in the Producer Gas.—If the producer tar contained 90 per cent. carbon, its hydrogen content was 10 per cent.

$$\frac{4,582,824 \times 0.526 \times 0.10}{1,000} = 241 \text{ kg. of hydrogen in the tar.}$$

8. Total Hydrogen in the Producer Gas.—The total amount of producer gas, passing "Sampling Station A" during the test, contained the following hydrogen:

As-free hydrogen.....	1249.1 kg.
In the methane.....	595.6 kg.
In the water vapor.....	278.5 kg.
In the tar carried in the gas.....	241.0 kg.
	<hr/>
	2364.2 kg.

9. Hydrogen from the Steam Supplied to the Producer.—Of the tar and soot deposited in the gas flue during the test, about 7 per cent. was hydrogen or, $268 \times 0.07 = 19$ kg. of hydrogen.

There was contained in the coal

$$32,106 \times 0.061 = 1958.5 \text{ kg. hydrogen.}$$

The hydrogen passing from the producer, other than that in the steam supplied for blowing was, therefore,

$$1958.5 - 19 + 135.7 = 2075.2 \text{ kg.}$$

$2364.2 - 2075.2 = 289$ kg. hydrogen from the steam or, $289 \times 9 = 2601$ kg. water, introduced into the producer, during the test, in the form of steam.

10. Heat Introduced into the Producer by the Steam.—As the pressure of the steam was 25 lbs. (gage) at the injector, the heat carried in, in excess of sensible heat of water at atmospheric temperature, was

$$2601 \times (646 - 24) = 1,617,822 \text{ Calories.}$$

11. Total Heat Introduced into the Producer.— $212,320,392 + 1,617,822 = 213,938,214$ Cal. = total heat (above 24° C) in coal, steam, and atmospheric moisture, introduced into the producer.

12. Heat Lost in the Ash.—From (2), there was 47.2 kg. of fixed carbon in the ash drawn from the producer.

$$47.2 \times 8100 = 382,320 \text{ Cal. in the ash.}$$

$$\frac{382,320}{213,938,214} \times 100 = 0.2 \text{ per cent. loss.}$$

13. Heat in the Dry Producer Gas.—The total weight of dry producer gas was 115,657 kg. The average temperature of the producer gas was 580° C and, as the temperature of the atmosphere was 24° C, the mean temperature between the two was 302° C.

Sp. ht.

CO ₂	0.1241	×	0.244	=	0.0303
O ₂	0.0117	×	0.214	=	0.0025
CO.....	0.2424	×	0.256	=	0.0620
CH ₄	0.0206	×	0.834	=	0.0172
H ₂	0.0108	×	3.581	=	0.0387
N ₂	0.5904	×	0.256	=	0.1513

0.3020 = specific heat of the dry producer gas at the mean temperature of 302° C.

$115,657 \times (580 - 24) \times 0.3020 = 19,420,198 \text{ Cal.} = \text{sensible heat in the dry producer gas.}$

CO $115,657 \times 0.2424 \times 2,436 = 68,294,302 \text{ Cal.}$

CH₄ $115,657 \times 0.0206 \times 12,200 = 29,066,917 \text{ Cal.}$

H₂ $115,657 \times 0.0108 \times 29,100 = 36,348,682 \text{ Cal.}$

133,709,901 Cal. = heat from combustibles in the producer gas.

$19,420,198 + 133,709,901 = 153,130,099 \text{ Cal.} = \text{total heat in the dry producer gas.}$

14. Heat in the Tar of the Producer Gas.— $319,319 \times 0.00756 = 2414 \text{ kg.} = \text{tar, carried past the "Sampling Station A," in the producer gas.}$

Sp. ht.

$2414 \times (580 - 24) \times 0.35 = 469,764 \text{ Cal.} = \text{sensible heat.}$

$2414 \times 8889 = 21,458,046 \text{ Cal.} = \text{heat of combustion.}$

219,27,810 Cal. = total heat in the tar.

15. Heat in the Soot of the Producer Gas.— $319,319 \times 0.00347 = 1108 \text{ kg.} = \text{soot carried past "Sampling Station A" in the producer gas.}$

Sp. ht.

$$1108 \times (580 - 24) \times 0.31 = 190,975 \text{ Cal.} = \text{sensible heat.}$$

$$1108 \times 8056 = 8,926,048 \text{ Cal.} = \text{heat of combustion.}$$

$$9,117,023 \text{ Cal.} = \text{total heat in the soot.}$$

16. Heat in the Water Vapor in the Producer Gas.—From (5), there was 2506 kg. of water vapor in the producer gas, 1221 kg. from the air entering the producer and the remainder (1285 kg.) from the steam and coal.

Figuring the sensible heat in 1221 kg. of water vapor above 24°C and the total (sensible and latent) heat in 1285 kg. water vapor above 24°C (using the formula $0.447 \div 324 \times 10^{-6}t$ for specific heat of water vapor)

$$1221 \times (580 - 24) \times 0.545 = 362,917 \text{ Cal.}$$

$$1285 \times 880 = 1,130,800 \text{ Cal.}$$

$$1,493,717 \text{ Cal.} = \text{total heat in water vapor.}$$

17. Total Heat in the Producer Gas at "Sampling Station A."—

$$\text{Heat in dry gas} \dots\dots\dots 153,130,099 \text{ Cal.}$$

$$\text{Heat in tar} \dots\dots\dots 21,927,810 \text{ Cal.}$$

$$\text{Heat in soot} \dots\dots\dots 9,117,023 \text{ Cal.}$$

$$\text{Heat in water vapor} \dots\dots\dots 1,493,717 \text{ Cal.}$$

$$185,668,649 \text{ Cal.} = \text{total heat above } 24^{\circ}\text{C.}$$

18. Producer and Flue Losses.—

$$\text{From (11), the total heat introduced into the producer} \dots\dots\dots = 213,938,214 \text{ Cal.}$$

$$\text{From (17), the total heat in the producer gas at "Sampling Sta. A"} \dots\dots\dots = 185,668,649 \text{ Cal.}$$

$$28,269,565 \text{ Cal.}$$

$$\frac{28,269,565}{213,938,214} \times 100 = 13.2 \text{ per cent. loss (including the 0.2 per cent. loss in the ash).}$$

19. Heat Lost in the Flue Gases.—From (2), the amount of carbon passing "Sampling Station A" in the producer gas was 20,993 kg.

The average analysis of the flue gases (Table 2) shows:

	Per cent.
CO ₂	10.49 (by volume)
CO.....	0.12
CH ₄	0.10

10.71 of carbon-bearing gases.

TABLE 2.—ANALYSES OF FLUE GAS.

Sample.....	A.	B.	C.	D.	E.	F.	G.	H.
CO ₂	4.1	4.3	8.7	11.4	11.5	12.8	12.7	13.6
O ₂	16.1	15.2	9.7	7.1	6.4	4.7	4.8	3.6
CO.....	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH ₄
H ₂
N ₂	79.8	80.5	81.6	81.5	82.1	82.5	82.5	82.8
Per cent. excess air	314.0	244.0	81.0	49.0	42.0	27.0	28.0	20.0

Sample.....	I.	J.	K.	L.	M.	N.	O.	P.
CO ₂	11.9	10.5	12.1	11.3	11.20	10.0	12.5	9.2
O ₂	5.7	6.7	5.4	5.7	4.0	3.7	0.0	0.0
CO.....	0.0	0.0	0.0	0.0	0.2	0.4	0.6	0.8
CH ₄	0.2	0.3	0.5	0.6
H ₂	1.1	2.1	3.2	4.2
N ₂	82.4	82.8	82.5	83.0	83.3	83.5	83.2	85.2
Per cent. excess air	35.0	44.0	33.0	35.0	15.0	9.0	—11.0	—14.0

$0.1071 \times 12 = 1.2852$ g. = weight of carbon in the carbon-bearing gases in one gram-molecular volume of flue gases at 0°C .

$$\frac{20,993,000}{1.2852} = 16,334,423 \text{ gram-molecular volumes of dry flue}$$

gas.

The weight of one gram-molecular volume of dry flue gas was

	Per cent.
CO ₂	$0.1049 \times 44 = 4.6156 = 15.500$
O ₂	$0.0618 \times 32 = 1.9776 = 6.650$
CO.....	$0.0012 \times 28 = 0.0336 = 0.112$
CH ₄	$0.0010 \times 16 = 0.0160 = 0.054$
H ₂	$0.0066 \times 2 = 0.0132 = 0.044$
N ₂	$0.8245 \times 28 = 23.0860 = 77.640$

Total, 29.7420 g. 100.00

$\therefore 16,334,423 \times 29,742 = 485,818 \text{ kg.} = \text{the total weight of dry flue gases.}$ As the average temperature of the dry flue gases was 344.7°C , and of the atmosphere 24°C the specific heat of the gases at the mean temperature (184°C) was

	Sp. ht.
$\text{CO}_2 \dots\dots$	$0.15500 \times 0.2239 = 0.0347$
$\text{O}_2 \dots\dots$	$0.06650 \times 0.2200 = 0.0146$
$\text{CO} \dots\dots$	$0.00112 \times 0.2507 = 0.0003$
$\text{CH}_4 \dots\dots$	$0.00054 \times 0.7456 = 0.0004$
$\text{H}_2 \dots\dots$	$0.00044 \times 3.5104 = 0.0015$
$\text{N}_2 \dots\dots$	$0.77640 \times 0.2507 = 0.1946$

$0.2461 = \text{specific heat of the dry gases.}$

$485,818 \times (344.7 - 24) \times 0.2461 = 38,342,831 \text{ Cal.} = \text{sensible heat in the dry flue gases.}$

$\text{CO} \dots\dots$	$485,818 \times 0.00112 \times 2,436 = 1,325,467$	Cal. in the uncon- sumed CO .
$\text{CH}_4 \dots\dots$	$485,818 \times 0.00054 \times 12,200 = 3,200,569$	Cal. in the uncon- sumed CH_4 .
$\text{H}_2 \dots\dots$	$485,818 \times 0.00044 \times 29,100 = 6,220,414$	Cal. in the uncon- sumed H_2 .

$10,746,450 = \text{Cal. heat in the uncon-
sumed com-
bustibles in the
flue gases.}$

$16,334,423 \times 0.8245 = 13,467,732 \text{ gram-molecular volumes of nitrogen in the flue gases.}$

Deducting the nitrogen in the producer gas as found under (6).

$13,467,732 - 2,420,398 = 11,047,334 \text{ gram-molecular volumes of nitrogen.}$

$\frac{11,047,334}{0.792} = 13,948,654 \text{ gram-molecular volumes of dry air,}$

which entered the kiln through the burners.

$\frac{13,948,654 \times 22.3}{1000} = 311,055 \text{ cu. m. of dry air at } 0^\circ \text{C.}$

$\frac{311,055}{273} = \frac{x}{273 - 24}$

$x = 338,400$ cu. m. dry air at 24°C .

$$338,400 \times \frac{756}{739.46} = 345,969 \text{ cu. m. of moist atmosphere at } 24^{\circ}\text{C}.$$

As there was present an average of 16.1 g. of water vapor per cu. m. of atmosphere (Fig. 7), $\frac{345,969 \times 16.1}{1,000} = 5570$ kg. of

water vapor entering the kiln with the air required for combustion and the excess air.

From (8), the total hydrogen in the producer gas was 2364.2 kg.

The hydrogen, other than that in the moisture, escaping the flue gases was

$$\begin{array}{rcl} \text{CH}_4 \dots\dots\dots & 485,818 \times 0.00054 \times \frac{4}{16} & = 65.6 \text{ kg.} \\ \text{H}_2 \dots\dots\dots & 485,818 \times 0.00044 & = 213.6 \text{ kg.} \\ & \hline & 279.2 \text{ kg.} \end{array}$$

Assuming that all of the free hydrogen found in the flue gases came from the producer:

$2364.2 - 279.2 = 2085$ kg. of hydrogen or 16,680 kg. of water vapor in the flue gases coming from the producer gas. $5570 + 16,680 = 22,250$ kg. of water vapor, which left the kiln in the flue gases in addition to that which came from the ware.

The moisture entering with the air at the producer and with the air for combustion at the kiln was $1221 + 5570 = 6791$ kg.

$22,250 - 6791 = 15,459$ kg. of water vapor evaporated or produced within the producer and the kiln.

$6791 \times (344.7 - 24) \times 0.507 = 1,104,272$ Cal. sensible heat above 24°C in the water vapor from the air.

$15,459 \times 740 = 11,439,660$ Cal. total heat above 24°C in the water vapor from the steam and coal.

$$\begin{array}{r} 38,342,831 \text{ Cal.} \\ 10,746,450 \text{ Cal.} \\ 1,104,272 \text{ Cal.} \\ 11,439,660 \text{ Cal.} \\ \hline \end{array}$$

61,633,213 Cal. = total heat lost in the flue gases other than that leaving in the water vapor from the ware.

$$\frac{61,633,213}{213,938,214} \times 100 = 28.8 \text{ per cent. loss.}$$

20. **Heat in the Mechanical and Hygroscopic Water.**—The kiln setting consisted of 71,706 brick, which weighed when burned 175,402 kg.

The ignition loss of the clay was 3.39 per cent.

$\therefore \frac{175,402}{1.00 - 0.0339} = 181,557 \text{ kg.} = \text{weight of the green ware set (dry basis).}$

The green ware as set contained 0.543 per cent. mechanical and hygroscopic water.

$\therefore \frac{181,557}{1.00 - 0.00543} = 182,548 \text{ kg.} = \text{weight of the damp green ware as set.}$

$182,548 - 181,557 = 991 \text{ kg.} = \text{mechanical and hygroscopic water in the ware.}$

Assuming the mean temperature of evaporation of the mechanical and hygroscopic water to be 125°C (the corresponding

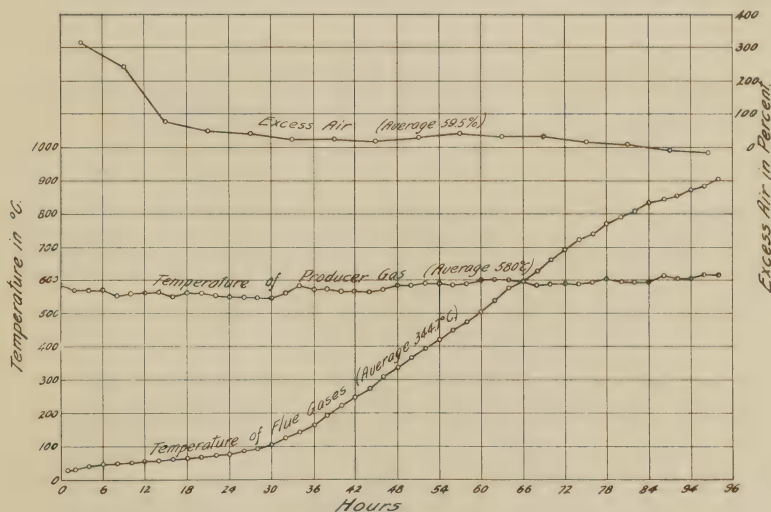


FIG. 8.—Producer gas and flue gas temperatures and excess air.

temperature of the flue gases (Fig. 8) being about 60°C), the heat leaving the kiln in this water vapor was

$$\begin{array}{rcl} 991 \times (125 - 24) & = & 100,091 \text{ Cal.} \\ 991 \times 522 & = & 517,302 \text{ Cal.} \\ \hline & & 617,393 \text{ Cal.} \end{array}$$

As this water vapor cooled down to 60°C , it gave up heat as follows:

$$\begin{array}{l} 991 \times (125 - 60) \times 0.477 = 28,812 \text{ Cal.} \\ \therefore 617,393 - 28,812 = 588,581 \text{ Cal.} = \text{net loss.} \\ \frac{588,581 \times 100}{213,936,214} = 0.3 \text{ per cent.} \end{array}$$

21. Heat Consumed in the Dehydration of the Clay and Leaving in the Vaporized Chemical Water in the Flue Gas.—From (20) the weight of the dry green ware was 181,557 kg. The burned weight of the ware was 175,402 kg.

$\therefore 181,557 - 175,402 = 6155 \text{ kg.} = \text{approximate weight of the chemical water.}$

The temperature of the maximum rate of dehydration of clays is about 560°C .

$$\begin{array}{rcl} 6,155 \times (560 - 24) \times 0.2 & = & 659,816 \text{ Cal.} \\ 6,155 \times 609 & = & 3,748,395 \text{ Cal.} \\ 6,155 \times 261 & = & 1,606,455 \text{ Cal.} \\ \hline & & 6,014,666 \text{ Cal.} \end{array}$$

The flue temperature corresponding to a kiln temperature of 560°C was (from curve—Fig. 8) about 150°C and the heat given up by this water vapor, on cooling from 560°C to 150°C , was

$$\begin{array}{l} 6,155 \times (560 - 150) \times 0.562 = 1,418,235. \\ \therefore 6,014,666 - 1,418,235 = 4,596,431 \text{ Cal.} = \text{net consumption.} \\ \frac{4,596,431 \times 100}{213,938,214} = 2.2 \text{ per cent.} \end{array}$$

22. Heat in the Ware at the End of the Burn.—At the end of the burn the temperature of the ware 4' above the floor

averaged 1135°C (Fig. 9), the temperature through the center of the crown was 1135°C , and the temperature at the floor level was 1070°C . Assuming that the level of 4' above the floor divided the mass of ware into halves, taking the temperature

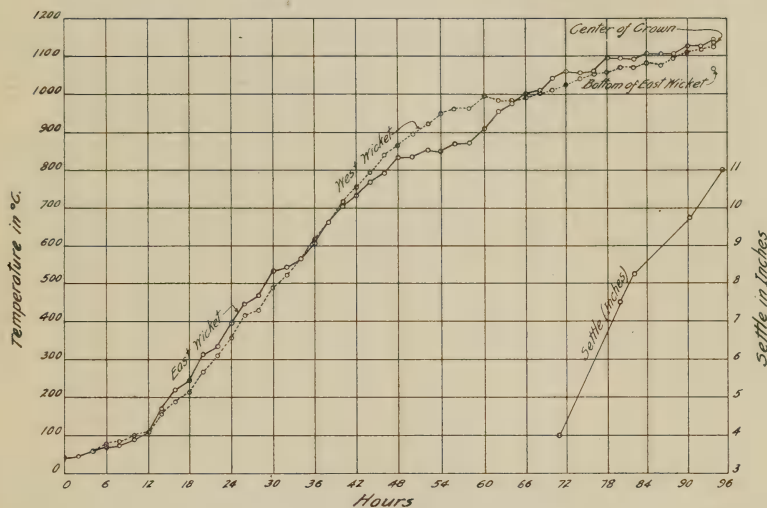


FIG. 9.—Internal Kiln Temperatures and Settle.

of the upper half as 1135°C and the temperature of the lower half as the average between 1135°C and 1070°C or approximately 1100°C , then the temperature of the whole mass can be considered as the average between 1100°C and 1135°C or 1118°C .

As the weight of the burned ware was 175,402 kg., the heat represented in this ware at the end of the burn was

$$175,402 \times (1118 - 24) \times 0.23 = 44,135,011 \text{ Cal.}$$

$$\frac{44,135,011 \times 100}{213,938,214} = 20.6 \text{ per cent.}$$

23. Heat in the Kiln Structure and in the Ground at the End of the Burn and the Radiation Loss.—The losses previously calculated amount to 65.1 per cent.

$100 - 65.1 = 34.9$ per cent. of the total heat was stored up at the end of the burn in the kiln structure and in the ground under and around the kiln and was lost by radiation during the burn.

As soon as the fires were cut off at the end of the burn, temperature readings of the external surface of the kiln were taken at numerous places on the crown and side walls, by means of a copper-constantan couple, of small gauge, and a potentiometer.

The average temperature of the exterior of the crown was 130°C , the exterior of the side wall above the hob 78°C , and the exterior of the hob 46°C . Knowing the internal and external temperatures, curves were drawn indicating the probable temperature throughout the cross section of the several parts and, from these, average mass temperatures were secured. Crown 477°C , side wall 429°C , and hob 423°C . Then, the heat contained in the kiln structure above the ground was as follows:

Crown.....	$49,432 \times (477 - 24) \times 0.23 =$	5,150,320 Cal.
Side wall.....	$45,562 \times (429 - 24) \times 0.23 =$	4,244,100 Cal.
Hob.....	$45,017 \times (423 - 24) \times 0.23 =$	4,131,210 Cal.

13,525,630 Cal.

$$\frac{13,525,630 \times 100}{213,938,214} = 6.3 \text{ per cent.}$$

The heat stored up in the kiln bottom and in the ground, below and around the kiln, and the heat radiated during the burn was

$$34.9 - 6.3 = 28.5 \text{ per cent.}$$

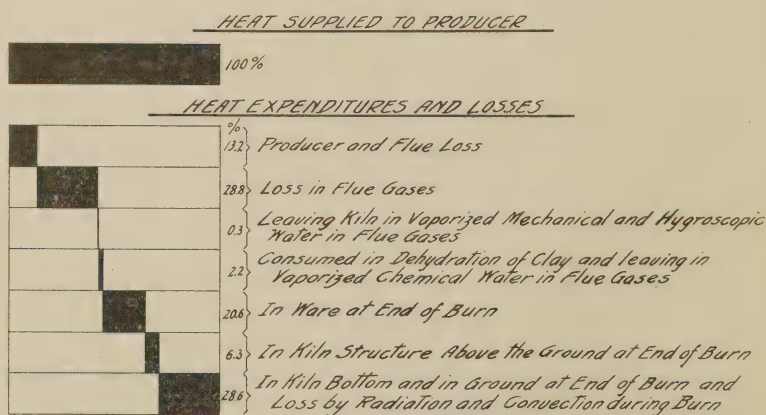


FIG. 10.—Heat Distribution.

V. Conclusion.

The coal consumption was 989 lbs. per 1000 brick.

No direct means was available for measuring the steam supplied to the producer, hence it was necessary to derive the amount by calculation. The results indicate that a smaller quantity of steam was used than in normal producer practice. This was to be expected, however, as the steam was cut off from the bosh and entered only through the center tuyère.

Using the external kiln temperatures, secured at the end of the burner, time-temperature curves were drawn indicating the probable surface temperatures throughout the burn for the several parts of the kiln. From these curves were secured the average temperatures as follows: Crown 74°C , side walls 41.6°C , and hob 31°C . Using the formula of Peclet for radiation and convection, the total radiation and the convection loss from the exterior surface of the kiln was calculated to be 4.8 per cent. This is undoubtedly too low and the figures were not included as a part of the calculation. However, attention should be called to the unusually low external kiln surface temperatures, which, together with the short duration of the burn, would necessarily result in a low radiation loss. In the author's opinion, the total radiation and convection losses from the kiln structure, including the burners, was not over 15 per cent. and possibly as low as 10 per cent.

The coal was elevated mechanically to the producer charging floor and all coal and ash handling was centralized.

The advantage of a clear kiln yard, with entire absence of coal and ash piles, need hardly be argued.

Where no space is necessary for piling coal, the kilns may be placed closer together, resulting in a more compact kiln yard.

As the producer and flue loss, as indicated in the calculation, was over 13 per cent., the use of a producer, from the standpoint of heat generation only, cannot be considered more efficient than the combustion of coal in the kiln furnaces, but an advantage lies in the ability to control the application of the gas to the kilns. This is brought out clearly by the record of excess air in the flue gases, indicated in Table 2 and Fig. 8. This air excess is much lower than in most direct-coal-fired kilns.

Either oxidizing or reducing conditions, to any degree, may be had at will and change from the one condition to another can be effected almost instantaneously.

Only a limited amount of solid fuel can be burned in direct-fired-kiln furnaces. Except by increasing the draft through the grates, the amount of fuel consumed can be increased only by increasing the grate area. In the gas-fired kiln, there is no such limitation, with the result that the heat application, at safe periods during the burn, can be made at a much greater rate than in the case of solid fuel direct-fired.

One burner and one producer man handled the burning in 12-hour shifts. The boiler fireman removed the ashes from the producer. On Sundays, the day burner looked after the boiler and removed the ashes from the producer, if necessary.

When the number of direct-fired kilns is increased to such an extent that one burner cannot take care of them, then the producer-gas-burning system would show a saving in labor, but there is no great relative reduction in labor for a small gas installation.

Producer gas has a lower flame temperature than coal, direct fired. Producer gas with its inert constituents—nitrogen, carbon-dioxide and water vapor—loses a considerable part of its sensible heat in traveling from the producer to the burners, in addition to the loss due to “cracking.” These inert gases, acting as a dilutant to the combustible mixture, reduce the resulting combustion temperature. In view of this, it is unreasonable to expect very high temperatures from producer gas, when using air at atmospheric temperatures to support combustion.

The advantages and disadvantages of this system may be summarized as follows:

Advantages:

1. Centralization of coal and ash.
2. Clean kiln yard.
3. Reduced kiln yard space.
4. Combustion control.
5. Generation of a large amount of heat in a limited furnace space.

6. Quick burns.
7. Labor saving when the capacity exceeds a one-man unit.

Disadvantages:

1. Producer and flue losses.
2. Lower flame temperature.

DISCUSSION.

MR. BLAIR: I would like to ask Mr. Harrop if his producer losses were offset by the better control of excess air in the kiln? You stated that the grate would burn with approximately 900 pounds of coal per 1000 brick. What could they do with coal combusted in the fire boxes direct? Could they do as well as that?

MR. HARROP: In my judgment, the saving due to the well-nigh perfect control that they were able to get in the way of excess air and the ease of manipulation of the combustion conditions would fully cover the producer losses. I am sure that if the saving in the reduction of excess air would not cover the producer losses, that the other advantages would. It could be calculated, quite readily, whether the expenditure of fuel to heat a normal amount of excess air over what we found, would equal or be in excess of 13 per cent. It would be very interesting to see whether it would cover or exceed the loss in the producer.

MR. MONTGOMERY: I would like to ask Mr. Harrop to please repeat his statement in regard to the maximum temperatures reached in a periodic kiln, using producer gas with cold air. He said something about reaching cone ten in the bottom of the kiln.

MR. HARROP: That was a continuous kiln which was being fired with a very poor grade of lignite, and the man who reached cone ten said he stopped the kiln, not because he could not reach a higher cone, but because he feared the kiln would be damaged.

MR. MINTON: I would like to ask, what was the height and diameter of the stack and how high were the inside walls?

MR. HARROP: The stack is 40 feet high and I think the division walls extend to the top of the stack.

MR. ORTMAN: It seems to me that a statement from Mr. Harrop as to his observations of the temperatures of the fire boxes in this case as compared with observations made on direct-coal-fired methods and the probable effect that the difference in temperature, if any, would have on kiln repair, might form a very valuable addition to the record in connection with this kiln.

MR. HARROP: This test was made about a year and a half ago—my remembrance is that there were no enclosed fire boxes, similar to those used for burning solid fuel, but that the hole or opening through the side wall was very small. There was a bag wall, to be sure, but I do not believe that the temperatures reached in what you might call the fire boxes are as high as the temperatures reached in the combustion of solid fuel.

NOTES ON THE HYDRATION OF ANHYDRITE AND DEAD-BURNED GYPSUM.

By A. C. GILL, Ithaca, N. Y.

In the prosecution of certain studies which, in accordance with the plans of the late H. E. Kramm, of Cornell University, were to have led up to an exhaustive discussion of the properties and conditions of the formation of gypsum and anhydrite, two experiments were inaugurated, the results of which have recently come to light. These seem worthy of record both on account of their intrinsic interest and as a tribute to the painstaking methods of Mr. Kramm. The object of this investigation seems to have been to determine the extent to which time might be a factor in the "setting" of anhydrite and dead-burned gypsum. As is well known, for short periods of time, these substances show little or no tendency to set.

The experiments were conducted in two wide-mouthed bottles or cylindrical jars having metallic screw-caps, but without rubber rings for air-tight sealing. Each jar was a little more than one and a half inches in diameter, and slightly less than six inches high, having thus a capacity of about 250 cc. In one was placed some 50 or 60 grams of anhydrite from Windsor, N. S., broken approximately fine enough to pass through a sieve of six or eight meshes to the inch. The other was charged with several lumps of Hillsboro, N. B., alabaster which had been heated for three and a half hours to a maximum temperature of 560°C , the lumps being an inch or more in greatest diameter, and having an aggregate volume of perhaps 60 or 75 cc.

Both bottles were filled with water and closed on Oct. 28, 1911. Late in 1917, a little more than six years after the beginning of the experiment, they were discovered with their carefully prepared labels still intact. A striking appearance was presented, as shown by the two photographs (Figs. 1 and 2) which were made after cutting off the tops of the bottles. The water

had entirely evaporated from both specimens. They may perhaps be best described separately.

I. Anhydrite. (See Fig. 1.)

The small fragments of anhydrite were so firmly bound together that it was impossible to pry them out for analysis without breaking to a coarse powder. Glistening crystals of gypsum could be seen in the interstices, and brilliant, acicular crystals, attaining a maximum length of about one-half inch, projected

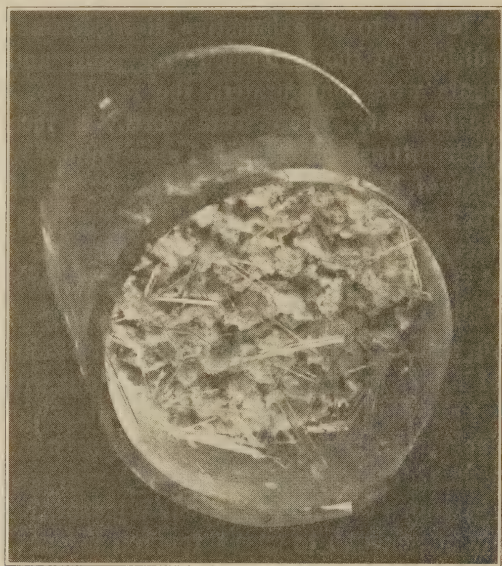


FIG. 1.

Consolidated anhydrite with gypsum needles, formed within a period of six years.

into the free space which had been occupied by the water. These crystals gave very good reflections on a Fuess goniometer, showing by their prism angle of $68^{\circ} 39'$, that they are elongated in the direction of the c axis.

In order to determine to what extent hydration had taken place, about half a gram (0.4475 g.) of the material was dug out with a heavy knife point, avoiding as far as possible the visible

gypsum crystals. On heating to constant weight at low red heat the loss was found to be 8.29 per cent. (37.1 mg.). This corresponds to a hydration into gypsum of 34.15 per cent. of the original anhydrite. It shows conclusively that the hydration was not limited to the amount of calcium sulphate which could be held in solution at one time, since all the water originally present would dissolve less than half a gram of that substance, while fifteen or twenty grams of the anhydrite must have been hydrated.

Unfortunately, no data is at hand to indicate how much of the "setting" was due to temperature changes, thus leaving in doubt the extent and rate of recrystallization which would take place at constant temperature. That the anhydrite fragments were firmly cemented by gypsum crystals, under the existing conditions, is fully established.

II. Dead-burned Gypsum. (See Fig. 2.)

The pieces of burned alabaster in the second bottle had become veritable porcupines with a complete covering of fine bristling gypsum needles about one-eighth of an inch in length. Inside the spiny coating, the mass had "set" to much greater hardness than ordinary plaster of Paris. By means of heavy forceps a portion was cut from one of the lumps, and, after the crystals were broken away from its surface, a water determination was made by the method of loss. Nearly a gram of the material (0.9865 g.) lost 18.8 per cent. (185.4 mg.). This indicates a re-hydration of 87.46 per cent. of the calcium sulphate of the burned gypsum. The difference in behavior between this substance and the anhydrite is very marked, the water seemingly finding its way back to its place in the dehydrated gypsum much more readily than it could make place for itself in the crystallized anhydrite. The smaller amount of water, larger amount of calcium sulphate, and the greater degree of hydration, make the argument against simple solution and subsequent evaporation even more compelling in this case than in that of anhydrite.

A further phenomenon should be noted as having a bearing on the significance of this experiment. The bottle was found to have a vertical crack from the top almost to the bottom. Through

it the water had evidently oozed and by evaporation a small amount of gypsum was deposited on the outside of the bottle. It seems almost certain that this crack was produced by the ex-



FIG. 2.

Fragments of "dead-burned" gypsum, with coating of recrystallized gypsum needles.

pansive force of hydration or by the growing force of the gypsum crystals. Mr. Kramm would hardly have used a cracked bottle and if the crack had existed during the whole of the experiment,

it would seem that the water would have escaped before producing such extensive changes. The crack would allow of more rapid desiccation, however, and this may explain the smaller size of the gypsum needles in this bottle.

The fact that, in both bottles the multitude of acicular crystals were all attached to the masses of introduced sulphate and none to the glass walls, would seem to corroborate Taber's view—that the crystals grow at the point of attachment rather than at the free end.

In conclusion, while emphasizing the fact that under the conditions of these experiments both natural anhydrite and "dead-burned" gypsum attained a firm "set," it may be pointed out that there is room for further investigation as to the rate at which this takes place, since no observation was made as to the time when evaporation was complete. Moreover, the question of the relative importance of temperature changes, causing supersaturation by cooling, and of constant temperature hydration and crystallization, due to the greater solubility of CaSO_4 than of $\text{CaSO}_4 + 2 \text{H}_2\text{O}$, is raised rather than answered.

COMMUNICATED DISCUSSIONS.

F. A. KIRKPATRICK: The hydration of anhydrite is interesting from a geological point of view. Certain gypsum deposits have evidently been formed by the weathering of the anhydrite which is found beneath the gypsum. The rate of hydration in nature is probably much slower than that observed in the laboratory, as the conditions in the latter case were very favorable for hydration. Anhydrite is not used as a material of construction since it hydrates and sets too slowly.

The hydration of burned gypsum presents a practical problem of great interest. There still remains a large amount of experimental work to be done along this line. The well-known investigation of Glasnapp on Hydraulic Gypsum should be extended to include strength tests. If we should accept Glasnapp's classification of burned gypsum products, the sample of Hillsboro alabaster heated for three and a half hours to a maximum temperature of 560°C would be completely dehydrated.

In contact with water it would show, in short periods of time, no hardening or only imperfect hardening. It would contain little or no hydraulic gypsum. In the long period of storage, about six years, the material used would hydrate and set slowly, probably mostly by crystallization. The introduction of alum or other catalyzers would decrease the time of set sufficiently to allow the material to be used for practical purposes.

W. E. EMLEY: Mr. Gill has established one point which is of great interest and importance to the gypsum industry, *viz.*, that both anhydrite and dead-burned gypsum will hydrate if given sufficient time.

The ordinarily accepted theory of the setting of gypsum, as applied in this case, would be that the water dissolves the anhydrous calcium sulphate which, subsequently, crystallizes out in the form of the less soluble hydrated gypsum.

Theoretically, a small amount of water could continue to dissolve anhydrite and deposit gypsum indefinitely. The quantity of water required is not at all dependent upon the solubility of the anhydrite, but depends solely upon the fact that the gypsum which is deposited carries with it two molecules of water for each molecule of calcium sulphate.

Mr. Gill leads one to infer that he believes his experiments have thrown some doubt upon the working of this theory; I cannot see that this is the case. I believe that the fact that his dead-burned gypsum hydrated to a greater extent than his anhydrite is due to the greater speed of reaction rather than to the relative quantities of water present. I believe that in both cases, the reactions continued until the water left as such was not sufficient to supply the two molecules necessary for the crystallization of the calcium sulphate held in solution.

The dead-burned gypsum was apparently more active than the anhydrite, and therefore was able to hydrate to a greater extent before the water had evaporated.

I believe that the experiment does prove conclusively that anhydrite and dead-burned gypsum will set; I believe that it also proves that dead-burned gypsum, formed under the conditions of the experiment, sets more rapidly than anhydrite.

I do not believe that the experiment throws any particular light on the mechanics of the setting, because the two most important elements were not observed, *viz.*, the time and the temperature.

A. C. GILL: The discussions of Messrs. Kirkpatrick and Emley lead me to emphasize the fact that the experiments with anhydrite and dead-burned gypsum were inaugurated and planned by Mr. Kramm. The present paper is merely an attempt to salvage some of the results which he would have attained if he had lived to complete the investigation.

Mr. Kramm doubtless intended the time and temperature of heating the Hillsboro alabaster to insure complete dehydration. He may even have carried out analyses to confirm this, though no such record is known to me. The possibility of using alum as an accelerator, as suggested by Mr. Kirkpatrick, is worthy of careful consideration.

As to Mr. Emley's discussion, it may be pointed out that the formation of gypsum crystals, to which the setting of the substances under investigation is supposed to be due, may take place from solution or simply by the addition of two molecules of water to each one of calcium sulphate, without the latter substance passing into solution. If from solution, it doubtless would go on at constant temperature when saturation for calcium sulphate was reached. But what the relative rate of setting would be at constant temperature, as compared with that produced by the diurnal temperature change of the laboratory, does *not* appear from the experiment. Nor is there any indication of the relative importance of setting without solution. Under the conditions of the experiment, it is certain that the relative quantities of water present may have had a great influence on the time required to reach saturation.

MEETINGS OF THE LOCAL SECTIONS, AMERICAN CERAMIC SOCIETY.

(Full accounts of all meetings should be sent to the Editor, Box 444,
New Brunswick, N. J.)

NORTHERN OHIO SECTION.

A meeting of the Northern Ohio Section was held in the afternoon and evening of June 10th, in Cleveland, Ohio. During the afternoon the following plants were visited:

Cleveland Metal Products Company, manufacturers of enameled lamp shades, stove parts, etc. The operations include pressing, oxyacetylene welding, electrical welding and enameling.

National Lamp Works, Euclid Glass Division, manufacturers of glass electric light bulbs. The points of interest were a Smith gas producer plant, the molding of glass melting pots and the manipulations in the manufacture of glass tubing and glass bulbs.

Nela Park Auditorium, Nela Park (Cleveland research laboratories of the General Electric Co.). An interesting illustrated lecture on the manufacture of electric lights was delivered by a member of the General Electric staff.

A joint meeting of the Section and the Cleveland Section of the American Chemical Society was held in the evening at the Olmstead Hotel. An instructive address on "Petrographic Studies in Ceramics" was delivered by A. A. Klein of the Research Laboratories, Norton Company, Worcester, Mass.

B. A. RICE, *Secretary*.

JOURNAL

OF THE

AMERICAN CERAMIC SOCIETY

A monthly journal devoted to the arts and sciences related to the silicate industries.

Vol. 1

February, 1918

No. 2

EDITORIALS.

UNITY AND ECONOMIC LEADERSHIP FOR THE CERAMIC INDUSTRIES.

The war has brought out rather strikingly the curious lack of unity of purpose among the several branches of our industry, even among those manufacturing the same general type of product. The absence of united action on the large economic questions confronting us to-day has been very apparent, especially in dealing with the several Governmental bodies which now control our industrial destiny. Even though some of our industries have organized more or less effectively, these associations have been lacking in cohesion and harmonious coöperation with allied ceramic branches. The result has been the failure of this important group of industries to secure representation on the War Industries Board.

It was only at the instance of a member of the Industrial Board, himself not familiar with the clay industries, that manufacturers of structural ceramic products were brought to the realization of the necessity for united action. This affords a striking lesson showing the need of a more general association of interests. In the American Ceramic Society we have already represented the technical interests of all the ceramic branches, but we must have an avenue also for the discussion of broad economic subjects and for concerted action when the occasion arises. This might be accomplished through the agency of this Society, perhaps through an Economic Section or through an

inter-organization of all the manufacturers' associations, a union céramique.

This brings up also the question of leadership. It is evident that the greatest amount of good can be accomplished only through the medium of broadly trained men for the positions of chairmen and secretaries of the different subdivisions, men who combine a thorough knowledge of business and markets with sound information concerning the general aspects of the important technical questions, such as those relating to fuel economy, labor-saving machinery, and last, but not least, concerning the great problem of labor. Such men are rare, and if they are not always available they must be trained for such work as far as is possible, by coöperation between the manufacturers and the colleges. It is evident that such individuals, to be useful, must not be clerks or salesmen, *per se*, but must be the resultant of a combination of those innate qualities which mark men of broad, human vision, and energy. Without such men, and we already have some in the industry, organized effort will prove to be a mere empty shell. *Ex nihilo nihil fit.*

ACID RESISTING ENAMELWARE.

The production of acid-resisting enamel-lined equipment in the United States has been subject to very definite wartime influences. These influences were felt soon after the outbreak of the war in August, 1914. Up to that time greater progress had been made in the manufacture of enameled steel apparatus for the various conditions of service ranging from the mild conditions encountered in the preparation of food to the severe mineral acid conditions encountered in the manufacture of gases, etc. Some cast iron equipment, lined with a relatively soft enamel, was produced at that time in this country, but most of the enameled cast iron wares used under the more severe chemical conditions were imported from Austria, Germany and France, particularly the latter country.

Shortly after the outbreak of the war, the manufacturers of acid-resisting enamel ware were confronted with two conditions: First, with the development of the dye and explosive industries there was a greatly increasing demand for acid-resisting

enamelware equipment. Second, the supply of the imported wares was greatly reduced, and the failure to secure a supply greatly inconvenienced some manufacturers who had standardized their processes with a view to the continued use of the cast iron apparatus of foreign design and manufacture. These conditions stimulated the production of domestic equipment and a marked improvement in the quality resulted but substitutes for the cast iron imported wares were not at first placed upon the market.

Owing to the heavy demands for steel plates in the munitions industries and later in the shipbuilding industry, a decrease in the quality of the plates available for the manufacture of enameled ware was noted for a time. Simultaneously with the decrease in quality of the plates the demand for high quality enameled apparatus for use in severe chemical service greatly increased. There appeared on the market at this time a small quantity of American made cast iron apparatus so constructed and enameled as to excel the wares formerly imported. The users of this type of apparatus quickly realized the merits of the cast iron ware manufactured in this country and the demand increased rapidly. It is at present available in units of quite large capacity, up to 200 gallons, and the limit has not been reached.

Since the outbreak of the war, an increased field of usefulness for enameled steel apparatus has been in the food industries and it is now used in the processing of materials whose mild corrosive action permits the use of relatively soft enamels. With the rapid expansion of the dairy industry and the increased manufacture of butter substitutes, including the hydrogenation of oils, large enameled steel units up to 5000 gallons capacity are in great demand.

It is gratifying to note that the acid-resisting enamel equipment industry is solving its problems in this time of effort. Manufacturers of pure food, explosives, gas for warfare purposes, pharmaceutical preparations, dyestuffs and of many other lines, find in the acid-resisting enameled iron wares a very useful and essential type of equipment.

The future of the acid-resisting cast iron branch of the enameling industry in this country is most promising.

ORIGINAL PAPERS AND DISCUSSIONS.

ON THE RELATION BETWEEN THE PHYSICAL PROPERTIES AND CHEMICAL COMPOSITION OF GLASS, VIII: MOLECULAR COMPOUNDS.

By EDWIN WARD TILLOTSON, JR.

This paper is an account of an attempt to secure information on the chemical compounds which are formed in glasses. The fundamental law which makes this possible has been extensively tested with mixtures of liquids and solutions and, without going into a mathematical demonstration, it may be said that theoretical considerations suggest that the refractive index of a mixture should be a linear function of the relative volumes of the components of the mixture, and this prediction is verified by the experimental data for a large variety of mixtures. When the refractive indices and the composition of a series of binary mixtures are plotted in a suitable manner, one or more straight lines are usually formed, the intersections of which, if there be more than one straight line, are interpreted as indicating the formation and the composition of the molecular compounds which constitute the mixture. This relationship, therefore, offers a means for obtaining information regarding the chemical condition of mixtures from which, because of the physical condition of the mixture, or of their own specific nature, the compounds formed therein may not be separated.

One of the most important applications of this law is in the study of glasses. Heretofore there has been no means by which the compounds present in a glass could be identified. Such investigations as have been carried out have been along two distinct lines: first, the behavior of glass surfaces toward reagents,

and second, the melting-point diagram of binary mixtures of comparatively simple and crystallizable silicates, borates, and phosphates.

The result of the former line of investigation has been the adoption of the following formula as typical and ideal for a normal glass: $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 6\text{SiO}_2$.¹ Although it may have been originally intended that this should represent merely the approximate composition of a good glass, the frequent use of this formula in chemical literature gives one the impression that a good glass should consist of a single chemical compound, and that a glass possessing this formula is such a compound, and therefore a typical and ideal glass. A careful examination of the data on which this formula is founded, fails, however, to reveal any convincing evidence that it represents a definite chemical compound; on the contrary, it appears to be an easily remembered composition in which has been combined a high resistance to the action of reagents, a small tendency to devitrification, and the possibility of melting it and of working it into the finished ware. These are the criteria by which this glass has been adjudged to be a chemical compound, the excellence of its properties as a glass.²

The second line of investigation, while scarcely more fruitful, is at least a more scientific method of attack, and results have been obtained which, besides being of theoretical interest, are of much practical importance. Yet such work must deal with crystallizable substances and gives information, so far as chemical composition is concerned, regarding only the crystallized material. Since little knowledge is at hand regarding chemical changes which may take place during crystallization, it is impossible to draw conclusions as to the chemical condition of the fused mixture or of the supercooled glass.

This paper is a record, primarily, of the results obtained in an

¹ See O. Schott, *Dingler's polytech. J.*, **216**, 346 (1877); Weber, *Ibid.*, **233**, 349 (1879); G. Wagener, *Ibid.*, **243**, 66 (1882); E. Tscheuschner, *Ibid.*, **256**, 75 (1885); Schwartz, *Chem. Zentr.*, **1886**, p. 825; Mylius and Foerster, *Ber.*, **22**, 1104 (1889).

² See Asche and Asche, "The Hexite-Pentite Theory," p. 253.

examination of the systems $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ and $\text{Na}_2\text{O}-\text{BaO}-\text{SiO}_2$ by means of the refractive index.

Table 1, however, contains data taken from the literature for the feldspar glasses and Table 2 similar data for the system $\text{CaSiO}_3-\text{MgSiO}_3$ (glasses). These data are shown in graphic form in Figs. 1 and 2. According to our hypothesis, since the refractive indices of the feldspar glasses lie on a single straight line, no new compounds are formed in this system. In the $\text{CaSiO}_3-\text{MgSiO}_3$ mixtures, however, three straight lines are obtained intersecting at two points, which is interpreted as indicating the formation of two new compounds, and from the position of the intersections, these compounds possess the compositions $\text{CaMg}_3(\text{SiO}_2)_4$ and $\text{Ca}_4\text{Mg}(\text{SiO}_3)_5$. It is of interest that no indication is given of the formation of diopside, $\text{CaMg}(\text{SiO}_3)_2$, although this is the only double silicate which crystallizes from these mixtures.¹ This system, therefore, apparently offers an excellent example of chemical changes which may take place during the process of devitrification of a glass. It is worthy of note that one of these new compounds possesses the chemical composition of the mineral tremolite, $\text{CaMg}_3(\text{SiO}_3)_4$. The specific gravities of these glasses give the same indications as the refractive indices as are illustrated in Figs. 1 and 2.

Experimental.

For the experiments described in this paper sodium carbonate, barium carbonate, calcium carbonate and a very good quality of glass sand were employed. The purity of each of the raw

TABLE 1.
Albite-Anorthite Glasses.

Anorthite. Per cent. by volume.	Refractive index. Na line.		Density.	
	Obs.	Calc.	Obs.	Calc.
0.00	1.4890	1.4890	2.382	2.382
31.85	1.5166	1.5166	2.483	2.483
48.32	1.5308	1.5308	2.533	2.536
65.16	1.5452	1.5453	2.591	2.589
82.39	1.5600	1.5602	2.648	2.644
100.00	1.5755	1.5754	2.700	2.700
	$dN/dp = 0.000864$		$dD/dp = 0.00318$	

¹ Allen and White, *Am. J. Sci.*, 27, 1 (1909).

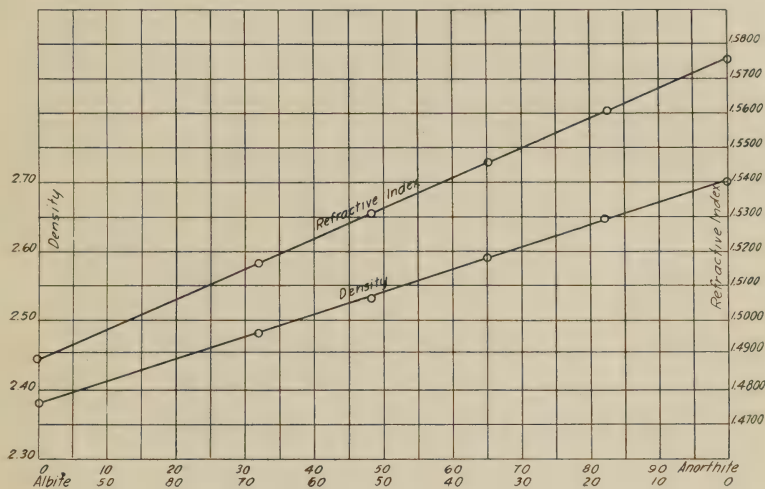


FIG. 1.—Albite-Anorthite Glasses.

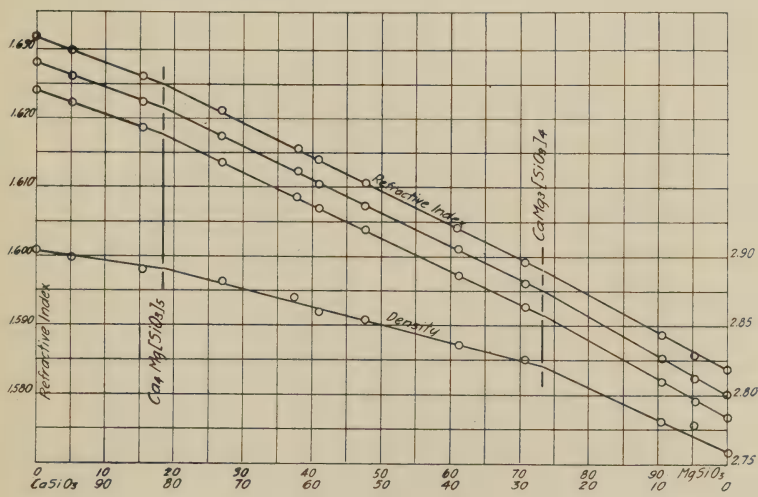
FIG. 2.— CaSiO_3 - MgSiO_3

TABLE 2.
CaSiO₃-MgSiO₃.

CaSiO ₃ . Per cent. by volume.	Refractive index. Na line.		Density.	
	Obs.	Calc.	Obs.	Calc.
0.00	1.5801	1.5801	2.758	2.760
4.76	1.5823	1.5828	2.777	2.771
9.54	1.5853	1.5854	2.781	2.781
28.92	1.5960	1.5960	2.823	2.822
38.76	1.6008	1.6008	2.835	2.834
52.35	1.6073	1.6073	2.854	2.851
58.75	1.6105	1.6104	2.858	2.859
62.80	1.6122	1.6123	2.872	2.865
72.99	1.6174	1.6172	2.881	2.877
84.60	1.6224	1.6224	2.891	2.891
94.75	1.6261	1.6261	2.899	2.899
100.00	1.6280	1.6280	2.904	2.904
	dN/dp .		dD/dp .	
	(0-26.78%)	= 0.000557		0.00225
	(26.78-81.45%)	= 0.000482		0.00125
	(81.45-100%)	= 0.000362		0.00086

materials was determined and on this basis the several mixtures were carefully weighed out, mixed and fused in hard burned clay crucibles in the oxidizing atmosphere of a gas furnace. After the glass was thoroughly fused it was poured out on cold iron plates, and after annealing, unless devitrification prevented, was broken up into small fragments. The refractive index for white light was measured with the aid of an Abbé refractometer, using selected fragments of the glass which presented a smooth and flat surface of the original plate. With a little care in selecting plane fragments of the glass, the values of the refractive index for successive plates usually agreed to within one or two units in the third decimal place and the average of a number of measurements was taken as the final value of the refractive index.

The System Na₂O-BaO-SiO₂.

In order that all the compounds formed in a ternary system may be identified, it is necessary that several series of mixtures be made, their number depending upon the number of compounds formed. The system Na₂O-BaO-SiO₂ serves to illus-

trate the procedure. Mixtures of Na_2O and SiO_2 were first made up. These varied in composition from $\text{Na}_2\text{O} \cdot \text{SiO}_2$ to $\text{Na}_2\text{O} \cdot 5\text{SiO}_2$. Beyond these limits either fusion was difficult or only crystallized products were obtained. This series indicates a compound of the $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$. The second series might well have consisted of mixtures of $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ and $\text{BaO} \cdot \text{SiO}_2$, but in order that de-

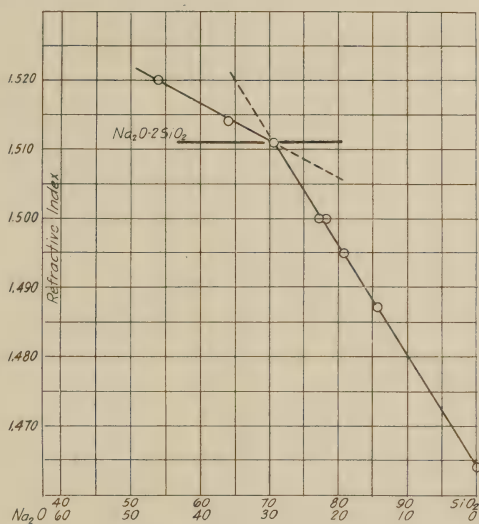
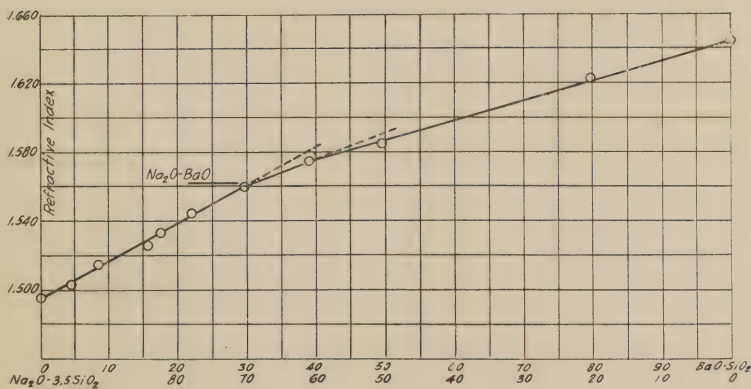


FIG. 3.

FIG. 4.— $\text{Na}_2\text{O} \cdot 3.5\text{SiO}_2$ — $\text{BaO} \cdot \text{SiO}_2$

vitrification might be eliminated as far as possible, and that the mixtures might approach more nearly to real glasses, $\text{Na}_2\text{O} \cdot 3.5\text{SiO}_2$ and $\text{Na}_2\text{O} \cdot 5\text{SiO}_2$ were used as variables with $\text{BaO} \cdot \text{SiO}_2$. In one series, $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ and $\text{BaO} \cdot 2\text{SiO}_2$ were the variables. In each of these mixtures the formation of a compound was indicated at molecular ratios for Na_2O and BaO of one to one. The final series was then made up in which $(\text{Na}_2\text{O} \cdot \text{BaO})$ and SiO_2 were the variables. This series indicates compounds of the formulas $\text{Na}_2\text{O} \cdot \text{BaO} \cdot 3\text{SiO}_2$ and $\text{Na}_2\text{O} \cdot \text{BaO} \cdot 4\text{SiO}_2$.

The data for these series are given in Tables 3 to 7, and are shown in graphic form in Figs. 3 to 7. In Figs. 4, 5 and 6 the existence of a compound is indicated in which the molecular ratio of Na_2O to BaO is one to one; in Fig. 7 this ratio of bases is maintained constant while the ratio of bases to SiO_2 was variable. The results, as shown in Fig. 7, indicate compounds of the composition $\text{Na}_2\text{O} \cdot \text{BaO} \cdot 3\text{SiO}_2$ and $\text{Na}_2\text{O} \cdot \text{BaO} \cdot 4\text{SiO}_2$. No compounds of this type, containing more than four molecules of SiO_2 , appear to exist in these glasses. The glasses possessing the composition of these compounds devitrify readily, the ease of devitrification increasing as the quantity of SiO_2 decreases. The series $\text{BaO} \cdot \text{SiO}_2$ was not extensively investigated, chiefly because of the high melting point and the readiness with which these mixtures crystallize. Two glasses were, however, made, corresponding in composition to $\text{BaO} \cdot \text{SiO}_2$ and $\text{BaO} \cdot 2\text{SiO}_2$, and, although the refractive index measurements for these glasses were subject to rather large errors, the indications are that $\text{BaO} \cdot 2\text{SiO}_2$

TABLE 3.
 $\text{Na}_2\text{O} \cdot \text{SiO}_2$.

Silica. Per cent. by volume.	Refractive index.
100.00	(1.464)
85.50	(1.4865) ¹
80.55	1.4950
78.00	1.5000
76.75	1.5000
70.70	1.5110
63.80	1.5137
54.20	1.5200

TABLE 4.
 $\text{Na}_2\text{O} \cdot 3.5\text{SiO}_2 \cdot \text{BaO} \cdot \text{SiO}_2$.

$\text{BaO} \cdot \text{SiO}_2$ Per cent. by volume.	Refractive index
0.00	1.4950
4.42	1.5030
8.44	1.5150
15.38	1.5255
17.69	1.5330
21.97	1.5440
29.80	1.5603
39.00	1.5750

¹ Extrapolated from Fig. 6.

TABLE 5.

 $\text{Na}_2\text{O} \cdot 3\text{SiO}_2 - \text{BaO} \cdot 2\text{SiO}_2$.

$\text{BaO} \cdot 2\text{SiO}_2$ Per cent. by volume.	Refractive index.
0.00	1.5000
6.82	1.5054
18.00	1.5200
25.70	1.5310
28.20	1.5330
33.20	1.5370
42.40	1.5488
52.20	1.5594
63.10	1.5718
74.70	1.5847
86.20	1.5945
100.00	1.6090

TABLE 6.

 $\text{Na}_2\text{O} \cdot 5\text{SiO}_2 - \text{BaO} \cdot \text{SiO}_2$.

$\text{BaO} \cdot \text{SiO}_2$ Per cent. by volume.	Refractive index.
3.96	1.496
7.42	1.504
11.46	1.515
17.43	1.526
23.95	1.541
32.0	1.555
42.3	1.571

TABLE 7.

 $\text{Na}_2\text{O} \cdot \text{BaO} - \text{SiO}_2$.

SiO_2 Per cent. by volume.	Refractive index.
49.5	1.6055
62.3	1.5755
64.15	1.5716
67.72	1.5684
70.64	1.5650
72.73	1.5603
74.77	1.5488
78.06	1.5407

is a definite compound. The two ternary compounds, therefore, correspond to double salts of the simple silicates $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ - BaOSiO_2 and $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ - $\text{BaO} \cdot 2\text{SiO}_2$.

The System $\text{Na}_2\text{O} - \text{CaO} - \text{SiO}_2$.

In Tables 8 and 9 and in Figs. 8 and 9 are presented data for the soda lime glasses. The series $\text{Na}_2\text{O} \cdot 3\text{SiO}_2 - \text{CaO} \cdot \text{SiO}_2$, as illustrated in Fig. 8, indicates the formation of a compound in which the ratio of Na_2O to CaO is two to three. Fig. 9 shows the series in which this ratio was maintained constant while the ratio of base to SiO_2 was varied. As will be seen from the figure, only one compound is formed, $2\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 7\text{SiO}_2$. Ordinary

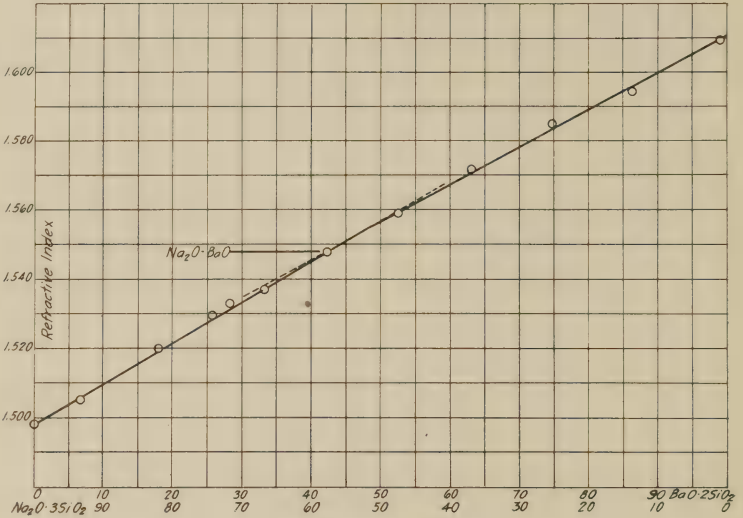


FIG. 5.

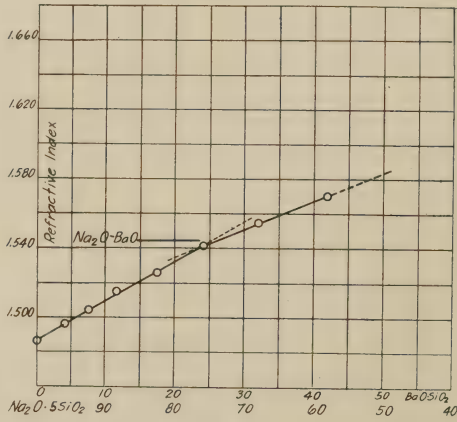


FIG. 6.

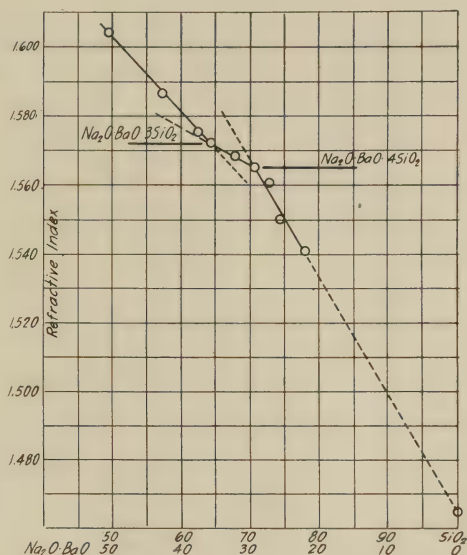


FIG. 7.

soda lime glasses contain much more soda and silica than correspond to this formula. On the one extreme a typical glass rich in alkali of a low melting temperature possessing a composition approximately represented by the following formula: $12\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 45\text{SiO}_2$. Such a glass is, therefore, considered to be made up of a solution of

$2\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 7\text{SiO}_2$	1 Mol.
$\text{Na}_2\text{O} \cdot 2\text{SiO}_2$	10 Mol.
SiO_2	18 Mol.

On the other extreme the high melting lime-rich glass of the "normal" formula $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 6\text{SiO}_2$ is considered as being a solution of

$2\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 7\text{SiO}_2$	1 Mol.
$\text{Na}_2\text{O} \cdot 2\text{SiO}_2$	1 Mol.
SiO_2	9 Mol.

TABLE 8.
 $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ – $\text{CaO} \cdot \text{SiO}_2$.

$\text{CaO} \cdot \text{SiO}_2$ Per cent. by volume.	Refractive index.
0.0	1.5000
4.35	1.5064
9.05	1.5115
14.60	1.5172•
20.98	1.5240
28.45	1.5330
37.40	1.5425
47.90	1.5590
61.50	1.5796

TABLE 9.
 $2\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot \text{SiO}_2$.

SiO_2 Per cent. by volume.	Refractive index.
60.50	1.5715
64.85	1.5645
68.25	1.5583
73.60	1.5425

It is of interest, although not considered to be of vital importance, to compare these results with the melting-point data of binary systems. According to Kultascheff,¹ the melting-point diagram of Na_2SiO_3 – CaSiO_3 mixtures exhibits a maximum, indicating a compound of the composition $2(\text{Na}_2\text{SiO}_3) \cdot 3(\text{CaSiO}_3)$. This was confirmed by the work of Wallace.² Wallace has also investigated the system Na_2SiO_3 – BaSiO_3 and has obtained data which indicate that these mixtures form an unbroken series of mixed crystals, and that no double silicate, therefore, separates from these fusions.

The melting-point diagram of the system Na_2O – SiO_2 does not appear to be on record. Investigations³ of “water glass” indicate that $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$, or some hydrate thereof, is the most acidic silicate of sodium which is stable in aqueous solution. Reasoning from analytical data, Legorio,⁴ in a study of crystallization in eruptive magma, concluded that the compound $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ might be regarded as the common solvent in such silicate fusions, and referred to it as the “glass base.” Of greater significance, however, is the observation of Gelstharp⁵ that all mixtures of silica

¹ *Z. anorg. Chem.*, **35**, 187 (1903).

² *Ibid.*, **63**, 8 (1909).

³ Lielegg, *Dingler's polytech. J.*, **153**, 44 (1859); Scheurer-Kestner, *Rep. Chem. Applique*, **5**, 150 (1863); Scherer, *J. prakt. Chem.*, **41**, 415 (1864); Kohlrausch, *Z. phys. Chem.*, **12**, 773 (1893); Mylius, *Ber.*, **VI Int. Cong. Appl. Sci.**, **1**, 677 (1908).

⁴ *Tscherm. Min. Mitteil.*, **8**, 421 (1886).

⁵ *Trans. Am. Ceram. Soc.*, **14**, 647 (1912).

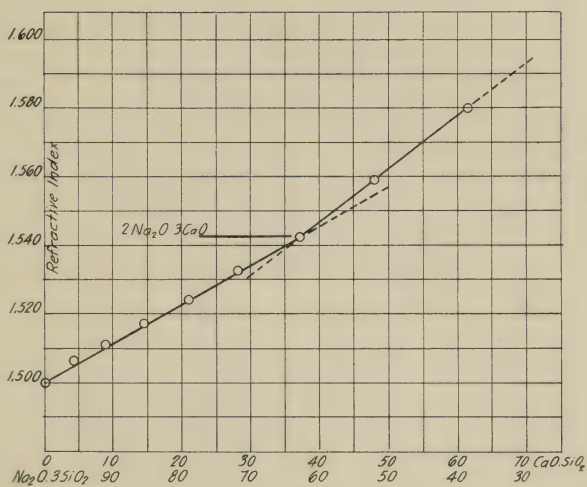


FIG. 8.

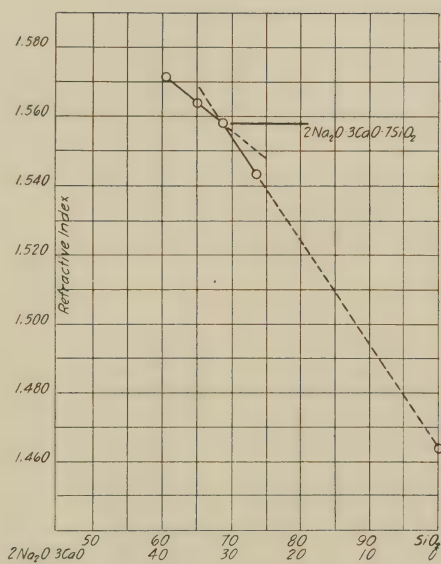


FIG. 9.

and sodium carbonate, which contained less silica than corresponds to the above formula, resulted in clear fusions when the reaction was complete, as evidenced by the cessation of the evolution of carbon dioxide. When, however, the quantity of silica was greater than that necessary to form $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$, undissolved silica was observed after the chemical reaction had gone to completion.

COMMUNICATED DISCUSSIONS.

C. H. KERR: All who have undertaken the study of any phase of equilibrium in silicate melts appreciate the great difficulties involved and any method which gives promise of opening up new lines of attack is exceedingly welcome. It seems that the present method offers great possibility of development as a new means of studying the problems of glass manufacture and it should prove equally valuable in other fields where the reactions are carried well on toward equilibrium.

In the present investigation, it is obvious that the whole field of non-devitrifying glasses, which can be made from the ingredients herein described, has not been covered, but it is not shown in the paper just what relation the compounds which have been studied bear to the entire field. It seems that a much more thorough investigation, at much closer composition intervals but embracing necessarily a greatly restricted number of compositions, would have yielded results of even greater value. There are not sufficient points on any one curve to show with any great assurance of correctness the nature of the curves and their significance.

In the context it is stated that the index for white light was determined. It is well known that the Abbé refractometer gives readings for the D line (or sodium line) of the spectrum.

As to the method of making index determinations, the specimens described are not considered to be satisfactory for the work in hand. The surfaces produced by pouring a glass melt onto an iron plate fall far short of being sufficiently good for readings of index in investigative work. Variations in index readings, due to surface irregularities, will, in many cases, exceed the varia-

tions due to the comparatively small changes in composition. Data are not submitted in detail showing just what variations in index were found in the individual readings on the same melt. It is a well-known fact that, even with a highly polished plano test piece, a very slight tipping up of one edge, due to a minute dust particle, will cause errors as great as one unit in the third decimal place, and surface irregularities of an ordinary fire polished specimen will show variations in index readings up to one or even two units in the third decimal place. The surface produced by pouring the melt onto an iron plate will probably cause even greater variations and therefore, with any reasonable number of readings, the variation due to surface is apt to be quite large. This must be borne in mind throughout the present work.

It is regretted that full tabulations of all readings are not recorded or, at least a full tabulation in one case, to show the actual mathematical probabilities. When it is realized that variations of one or two units in the third decimal place may occur in the individual readings, and probably errors as large as that due only to the irregular surface of the specimen, and still at the same time variations of a few units in the fourth decimal place are taken to indicate departure from a straight line, hyperbolic or other simple curve form, it is evident that a very careful consideration must be given to each factor influencing each deduction before it can be considered as established that the existence of definite compounds is shown.

Mr. E. D. Tillyer, of the American Optical Company, has given some consideration to the mathematical side of the problem. Taking the data in Table 2 and using the Cornu interpolation formula, he says that the probable error in the assumption of this formula (that an hyperbolic curve will fit various points on the chart) is substantially the same as the probable error from the assumption that three intersecting lines accurately represent the facts as in Fig. 2, given by the author. In other words, an hyperbolic curve, drawn through these points, is of the same order of probability in its correctness as are the three intersecting straight lines and, obviously, the hyperbolic curve would indi-

cate nothing, so far as we are now aware, about the existence of any definite compounds. Furthermore, the hyperbolic curve is the simplest physical expression we can conceive to indicate progressive changes in index of refraction or in other wave-length manifestations. I am greatly indebted to Mr. Tillyer for his consideration of these points.

These facts are not presented to show that the author's conclusions are in error, which is neither claimed nor denied, but merely to direct careful study regarding the mathematical significance of the data presented.

One further point to which attention should be drawn is the desirability of making greater use of the specific gravity determinations. The Lorenz-Lorentz formula has demonstrated that specific gravity changes must necessarily accompany changes in the indices of refraction. It is well known that the accuracy obtainable in specific gravity determination is several times the accuracy of determinations of the indices of refraction and, therefore, a study of the specific gravity variations in such connections as the present appears to offer very attractive possibilities.

A. E. WILLIAMS, C. C. RAND: It has been our experience in making experimental glass melts, even in quantities as small as 200 grams, that the glass cannot be made homogeneous enough to obtain an index of refraction which is more accurate than one point in the second place, by simply melting the mixture thoroughly. The glass must be stirred for a considerable time before an index correct to the third place is possible. Furthermore, the change of index due to volatilization is considerable and may cause a difference of one point in the second place between an experimental melt and a 1000-pound melt of identically the same batch composition.

If the compositions of the glasses for which the indices and densities are given are the batch compositions rather than the analyses after melting, we believe that the variations in the curves are within the limits of error possible from unhomogeneity in the glasses and changes of composition due to volatilization.

E. W. TILLOTSON: The questions raised in these discussions are those which naturally present themselves to those who have worked in this field. It is to be recognized that some error is present by reason of lack of homogeneity, and possibly as a result of volatilization. It was the purpose that errors from these sources were to be minimized by carrying out each experiment, as far as possible, under the same conditions. While the values for the indices given may not be absolute values and may differ from those secured in larger melts, it is believed that they are comparable among themselves within the limits mentioned.

The method of making the index determinations was, perhaps, not presented clearly. While the glasses were poured on iron plates, it was the upper "fire polished" surface which was used for making the measurements. By breaking the plate several small pieces could be obtained, with surfaces suitable for the fifteen or twenty readings taken.

With regard to the theory of the "straight line" relationship, the following illustrates the mathematical considerations:

Let $u_1, n_1, t_1; u_2, n_2, t_2$, etc., represent the velocity of light, refractive index and time required for light to traverse the distance l_1, l_2 , etc., of the several components, and L, U and T be the corresponding quantities for vacuum. The following relationships then follow:

$$\begin{aligned} \frac{U}{u_1} &= n_1 & \frac{U}{u_2} &= n_2 + \text{etc.} \\ t_1 &= \frac{l_1}{u_1} & t_2 &= \frac{l_2}{u_2} + \text{etc.} \\ T &= \frac{L}{U} \\ n_1 &= \frac{t_1}{T} & n_2 &= \frac{t_2}{T} + \text{etc.} \end{aligned}$$

If now the mixture be considered to be made up of an infinite number of layers through all of which the light must pass consecutively, and since

$$L = l_1 + l_2 + \text{etc.},$$

the time required for light to traverse the mixture will be

$$i_1 + i_2 + \text{etc.}$$

The refractive index of the mixture will then be

$$\begin{aligned} N &= \frac{(i_1 + i_2 + \text{etc.})}{T} = \left(\frac{l_1}{u_1} + \frac{l_2}{u_2} + \text{etc.} \right) \left(\frac{U}{L} \right) \\ &= \left(\frac{l_1}{L} \right) \left(\frac{U}{u_1} \right) + \left(\frac{l_2}{L} \right) \left(\frac{U}{u_2} \right) + \text{etc.} \end{aligned}$$

Substituting for $\frac{U}{u_1}$, $\frac{U}{u_2}$, etc., their equivalents n_1 , n_2 , etc., and for $\frac{l_1}{L}$, $\frac{l_2}{L}$, etc., the percentages by volume p_1 , p_2 , etc., the equation becomes

$$N = p_1 n_1 + p_2 n_2 + \text{etc.}$$

This indicates, therefore, that in mixtures, in which no new compounds are formed, the refractive indices would be expected to follow the "straight line" law, when the composition of the mixtures is expressed in *percentages by volume*. When new compounds are formed quantitatively in the mixture, it is to be expected that the linear relationship will still hold, but the indices may lie on several straight lines which intersect at compositions corresponding to those of the new compounds.

It may be added that nearly all of the data here presented was secured before the linear relationship between index and composition by volume became apparent. However, before it was adopted, confirmatory evidence was sought in published data on solutions and on mixtures of liquids. Nearly one hundred systems were recomputed on the volume percentage basis, and many systems were found in which the linearity is so striking as to make it difficult to believe that it is accidental. It is also difficult to explain, by the laws of chance, that the data should lie so nearly on straight lines which intersect at compositions corresponding to simple molecular ratios. If the true "curve" is hyperbolic or if the errors of experiment are so great as to mask the true curve, it is remarkable that the indicated linearity should present itself with such regularity. Incidentally, the writer is not aware that he has taken "variations of a few units in the fourth decimal place to indicate departure from a straight line."

With reference to the use of interpolation formulae, it is to be recognized that any "curve" may be approximated as closely as may be desired by the judicious selection of a formula of a sufficient number of terms. The fact that such an empirical expression may approximate a given series of points does not militate against a second expression which is founded upon a theoretical consideration of the problem and which gives an equally good agreement with the series of points in question. The hyperbolic function may be the most simple expression relating changes of refractive index with varying wave lengths or with varying temperatures, but it is not apparent that it should relate change in the index with changes in composition.

The statement that "specific gravity changes must necessarily accompany changes in the index of refraction" is true only under certain conditions. The formula of Lorenz-Lorentz relates the index with the density of a substance of given composition, under different conditions of temperature. In the systems under consideration, the temperatures remain substantially constant while the composition varies. It may be true that a glass of the highest density will have the larger index, but this is not universally true of mixtures in general. Mixtures of water and pyridine, for example, illustrate the reverse condition.

	D_{25}^{25}	$N_d, 25.2^\circ$ ¹
Water.....	1.000	1.33266
Pyridine.....	0.976 ²	1.50677

In this system the mixtures of the lower density have the higher index.

It is the writer's belief that the data here presented indicates a new line of attack for investigations on the constitution of glasses and other solutions, and it is to be hoped that others may subject the principles indicated to a minute experimental investigation.

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¹ Zawidski, *Z. phys. Chem.*, **35**, 129 (1901).

² Van Nostrand's Chemical Annual.

FIRE CLAYS IN NORTHERN IDAHO.

By E. K. SOPER, Corvallis, Oregon.

Location and Accessibility.—During the past three years there have been several important discoveries of high grade fire clay in Latah County, Idaho. Latah County is in the northwest part of the State, adjoining Whitman County, Washington. The clay deposits occur near Moscow, the County seat, and site of the University of Idaho. The deposits lie in close proximity to the Lewiston branch of the Northern Pacific Railway, and at the property of the Moscow Fire Brick and Clay Products Co., near Moscow, a railroad spur is being built to the clay pits to permit of the loading of the clay direct from the pit to the cars.

Geology of the Clay Deposits.—The geological occurrence of the clay deposits is interesting and some rather unusual features are exhibited. The fire clay is of the residual type, and has been derived from the weathering and decomposition of granite and associated pegmatite dikes. In addition to these fire clays there are other residual clays derived from the decomposition of basalt, which occurs over a large area in this region as a capping on top of the granite. The clays derived from the decomposition of the basalt are red, yellow or brown in color. Because of the higher percentage of iron and other fluxing impurities, they have little value for refractory purposes, but are excellent for the manufacture of brick, tile and other structural clay products. The fire clays are usually white or cream colored, and are white burning.

The general geology of this section of Idaho is comparatively simple. The rocks in the vicinity of Moscow consist of granite, quartzite, and basalt. The quartzite, which is the oldest rock, probably Algonkian in age, has been altered to a quartz schist in places. The granite occurs as a large intrusion into the quartzite and quartz schists and is probably of Cretaceous age. It forms the edge of the enormous granite batholith which, because of erosion, is now exposed at the surface over many square miles in the mountainous region to the east and southeast. The

quartzite and associated pre-Cambrian sediments have been mostly eroded from the region under discussion, but large areas are exposed to the northeast.

The basalt occurs as a flow, or series of flows, which originally covered the entire region of the Snake River plains in Idaho, Eastern Washington, and a large part of Eastern Oregon. This formation is known as the Columbia basalt and is probably of Miocene age. The lava flows originally reached well up on the foothills and lower western flanks of the mountains to the east of Moscow. Subsequent erosion has removed the basalt capping from many of the upper slopes of the foothills bordering the mountains and it is along the contact of this basalt cap-rock and the denuded granite that the fire clays and associated basaltic residual clays occur. Although there are large areas of granite, just east of this contact, from which the basalt has been completely removed, no important deposits of fire clay have been discovered as yet on these terrains.

The occurrence of the clay along the contact zone is probably due to the fact that on the granite side of the contact the hills rise to considerably higher elevations with rather steep slopes and the clay and decomposed granite is rapidly removed by erosion. Along the contact zone the slopes are more gentle and thus clay deposits of considerable thickness have accumulated. Another probable reason for the close association of the clay deposits and the zone of contact between granite and basalt suggested itself to the writer in examining one of the recently exposed clay banks near the town of Troy. At this locality the clay is overlain by a bed of volcanic tuff (consolidated volcanic ash), which, in turn, is partly overlain by basalt. At this place the tuff is exposed in immediate contact with the underlying residual fire clay which grades downward into partially decomposed granite. For a thickness of several feet beneath the tuff the clay is stained dark brown or yellow and contains numerous altered fragments of wood, showing plainly the existence here of an old weathered surface antedating the volcanic activity which resulted in the deposition of the ash. This evidence points to the conclusion that in some cases the residual clay was formed before the lava flows which now cover so much

of the region. Recent erosion of the lava capping has resulted in the exposure of the clay and decomposed granite and this in turn has been rapidly removed because of its relatively weaker resistance to erosion processes. The more rapid erosion of the areas of decomposed granite would tend to remove the clay except along the zone adjoining the contact, where the protecting capping of basalt, or tuff, has not been removed sufficiently long to result in the erosion of the clay. It is probable that much of the fire clay is Miocene or pre-Miocene in age, but as considerable decomposition of the granite has taken place since the erosion of the basalt, this has probably resulted in the formation of post-Miocene residual clay deposits.

The red, yellow, and brown clays which have been derived from the decomposition of the basalt are clearly of recent age. As would be expected, these generally occur at somewhat higher elevations than the white fire clays and in some cases are found directly overlying the fire clay. Recent erosion has resulted in the accumulation of secondary deposits of mixed sedimentary clays derived from the removal and mixing of the residual fire and basaltic clays.

The granite from which the fire clay in this locality has been derived is rich in feldspar, and generally contains only small amounts of hornblende, biotite or other ferro-magnesian minerals. In the vicinity of Moscow, the granite shows almost no mica and hornblende. Considerable white mica occurs in the granite at some places and there is also a segregation of the feldspars along narrow zones cutting through the granite in various directions. This has resulted in the occurrence of numerous narrow streaks of almost pure kaolin cutting the clay deposits. Narrow pegmatite dikes are also of rather frequent occurrence in the granite of this locality and this pegmatite has contributed additional amounts of kaolin to the fire clay. Because of the numerous segregations of the feldspar, white mica, or quartz constituents of the granite, the material resulting from the decomposition of the granite is often "spotty" in its occurrence. In places this material will consist almost entirely of sub-angular quartz sand. In other places, large amounts of partially de-

composed mica were noted, especially at the O. K. Olsen mine near Troy. In some places, where the proportion of feldspar in the original granite was high, deposits of good white fire clay have resulted from the weathering of the rock.

Extent of the Clay Deposits.—The size and shape of the clay deposits are variable. They range in thickness from a few feet to 40 or 50 feet, and the area of the deposits may vary from a fraction of an acre to 40 or 50 acres. This variation in size and shape is to be expected from the method of origin of the deposits, and from the character of the parent rock. In prospecting or developing these deposits, it is advisable to put down a large number of bore holes or test pits, arranged on some systematic plan, in order to obtain accurate data from which the extent of the deposit may be outlined.

Quality of the Clay.—The fire clay is of excellent quality and is well suited for the manufacture of fire brick. The best and purest deposits are those being worked at Moscow. Heating tests have shown that the clays have softening points ranging from that of Cone 30 to Cone 36. As the material comes from the pits, it develops only a moderate degree of plasticity and is of coarse texture, containing numerous angular grains of quartz embedded in white kaolin. There is sometimes present small amounts of white mica but in the Moscow deposits the quantity of mica in the clay is negligible. The kaolin is often rather dry and powdery, which makes the clay crumble easily, but when water is added and the material thoroughly mixed, the clay develops a surprising degree of plasticity. Up to the present time, no attempts have been made to utilize these clays for any purpose other than in the manufacture of fire brick and other refractory shapes. However, if the clay were washed, kaolin and silica of very good quality should result. The former might be utilized in the manufacture of pottery and other high-grade wares, and the white quartz, which is of unusual purity, might be of value in the manufacture of silica brick.

Development and Market.—The discovery of the fire clays of this locality is of recent date, but already two plants are in

operation manufacturing refractories. The plant of the Moscow Fire Brick and Clay Product Company at Moscow, Idaho, was placed in operation in 1917 and from the start this company has been operating continuously. Another plant is in operation at Troy, Idaho, about 10 miles east of Moscow. There are also brick plants at Mica and Freeman, in Spokane County, Washington, northwest of Latah County, Idaho. These Washington plants are operating on clays of similar origin to those here described. The market for fire brick and other refractories in the Northwest is very encouraging. The large smelters at Kellogg, Idaho; Northport, Washington; Tacoma, Washington, and in British Columbia, furnish a regular market for large quantities of refractories in addition to the amounts regularly used in the various industrial works at Spokane, Seattle, Tacoma, Portland, Vancouver, and other points in the Northwest.

It is not unlikely that a steel plant will be erected on the north Pacific coast in the near future, affording an additional market for fire clay and other refractory products. The Moscow Fire Brick and Clay Product Company is also utilizing deposits of the residual basaltic clay, which occurs on their property, in the manufacture of brick, tile and special shapes. Several varieties and colors of this type of clay occur in the Moscow deposit, and by their mixture with variable quantities of the fire clay, a wide range of red, buff, brown, and spotted brick and other products can be produced.

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GROUND COAT ENAMELS FOR CAST IRON.¹

By HOMER F. STALEY, Ames, Iowa.

The function of a ground coat enamel is that it should serve as a bond between the cover enamel and the iron and also protect the iron from oxidation while being heated to the temperature at which the cover enamel fuses. Statements are sometimes found in the literature that a ground coat is not necessary when powdered enamels are used for cast iron.² While it is sometimes possible to enamel a trial piece without the use of a ground coat, the percentage of good pieces obtained in this way is very small and the process is not a commercially feasible one. At the present time ground coats are universally used in the enameling of cast iron in this country.

It was formerly the practice to use very refractory ground masses which were merely sintered onto the iron but were not fused to a glass. The object was to produce a porcelain-like coating on the metal, toward which the cover enamel would act as a glaze. This type of ground coat is still used for wet-coat enamels on cast iron but for the powdered enamels it has been superseded to a large extent by thin glossy ground coats.

The basis of these sintered ground coats was a frit prepared from flint and borax, or from flint, feldspar and borax, with small additions of lead or sodium oxides. To this frit, clay and flint, or clay and feldspar, were added in sufficient quantities to make the refractoriness of the mass such that it would sinter, but not fuse in the enameling oven. Magnesium oxide or sulphate was used in small quantities to assist in floating the enamel. The ground coat was fired until it could not be rubbed off with the fingers and until the individual grains appeared rounded when

¹ By permission of the Director, Bureau of Standards.

² Holdcroft, H., *Jour. Soc. Chem. Ind.*, 29, 123.

examined with a good hand glass.¹ Formula No. 1 is a ground coat of this type which has been used in this country in the preparation of wet coat enamels. Further examples can be found in *Randau*, pages 124 and 125.

In the use of glassy ground coats, enamel makers have discarded the idea of there being an analogy between the enameling of cast iron and the glazing of porcelain and have attempted to produce glasses that would afford the maximum adhesion between the enamel and the metal. A satisfactory ground coat of this class should melt at a dull red heat, in order to protect the iron from oxidation; should be able to dissolve any oxides or foreign matter on the surface of the metal; should be sufficiently fluid to flow in part, into the minute pores of the metal, so as to produce a good bond, and should not blister or volatilize (burn off) until temperatures above those commonly employed in enameling furnaces are reached.²

The mixtures commonly employed in preparing the frits for this type of enamel are flint or sand, feldspar, borax, red lead and sodium nitrate. Flint and feldspar are the refractory ingredients of the enamel and supply the silica essential to the production of a permanent glass. Flint or sand is often used alone as the refractory component, especially in the older formulae, but many recipes call for the use of some feldspar in addition to the flint. Borax is used in the largest proportions as a flux on account of the ability of boric oxide to dissolve iron and other oxides. A ground coat glass high in boric oxide readily dissolves any small amounts of iron oxide present on the surface of the iron. Lead oxide is used because its compounds melt at low temperatures and produce fluid glasses having good mechanical strength when cold. The small amount of sodium nitrate is introduced in order to secure the oxidizing effect of the nitrate radical which prevents the reduction of the lead and the absorption of injurious sulphur gases by the glass during the fritting process. Small amounts of other fluxes such as fluorspar, cryolite,

¹ Paul Randau, "Enamels and Enameling," 2nd English edition, pp. 20 and 148, Scott Greenwood & Co.

² *Trans. Am. Ceram. Soc.*, 13, 531 (1911).

barium oxide, soda ash, etc., are sometimes used, but these perform no distinctive service and most of the enamel frits are compounded from the above list of materials. Small amounts of magnesium carbonate and magnesium sulphate are sometimes used in enamel frits on the assumption that they aid in the adhesion of the ground coat to the iron.¹ Cobalt oxide in small amounts is employed in many enamel frits for the same purpose.

As a raw material to be added at the mill, clay is invariably used on account of its ability to cause the enamel composition as a whole to remain in suspension. It also serves as a refractory ingredient and, in some cases, is the only raw refractory material introduced. Flint and feldspar are occasionally used as raw refractories. Magnesium carbonate, magnesium sulphate, borax, lime water, ammonia, etc., are used in small amounts to assist in floating the enamel. Sometimes a little raw cobalt oxide is added in cases where it has not been convenient to include in the frit.

The function and value of cobalt oxide in ground coats for cast iron is a debatable question. After a careful investigation of the subject, Coe came to the conclusion that "the use of cobalt oxide in a ground coat for cast iron enamels is of doubtful value."² On the other hand, manufacturers of sheet steel enamels in general claim that they cannot produce a satisfactory ground coat without the use of cobalt oxide or some other metallic oxide as a substitute for the cobalt. The remarkable effects claimed for the very small amounts of cobalt oxide added are not accounted for, and various unproven theories are advanced in an attempt to explain the phenomena.³

Since many excellent ground coats contain no cobalt, it is evident that cobalt oxide is not essential to the production of a satisfactory ground coat for cast iron. On the other hand, various factors enter into the production of satisfactory enameled iron ware and it is very difficult to determine the effect of the presence of cobalt oxide in the ground coat. As a result many

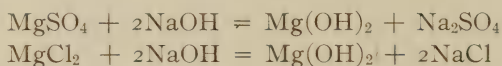
¹ Paul Randau, "Enamels and Enameling," p. 126.

² *Trans. Am. Ceram. Soc.*, 13, p. 545 (1911).

³ R. D. Landrum, *Ibid.*, 14, pp. 756-763 (1914).

enamellers, including the writer, in some instances use cobalt oxide in the preparation of ground coats because they feel that it is not detrimental and may possibly be beneficial. The cost of the cobalt oxide, compared to the value of the ware produced, is so small that its elimination from the formulas is not advisable.

As demonstrated by Ernest Mayer for glazes,¹ the settling of enamels is due to an excessive alkalinity of the enamel solution. Mayer divides the materials used for the flotation of slips into those whose action is physical and those whose action is chemical. In the first group are clay, syrup, gum arabic, dextrine, milk and blood. The two latter soon curdle and make quite thick suspensions. In the chemical group are various acid substances, including boric acid, vinegar, hydrochloric and sulphuric acid, which reduce the alkalinity by neutralizing a part of the alkali. A more effective group of chemicals are those which neutralize a part of the alkalinity and at the same time produce a flocculent precipitate. The most commonly employed are magnesium sulphate and magnesium chloride:



It is a noteworthy fact that not one of these chemical vehicles has any appreciable coagulating effect unless clay is present. It would appear, therefore, that the effect of these reagents is to coagulate the clay and thus render it capable of floating the other enamel ingredients. By the addition of acid substances, the enamel suspension would be rendered acid or faintly alkaline, a condition which is favorable to coagulation. By the addition of magnesium salts, the alkalinity would be reduced, a flocculent precipitate, $\text{Mg}(\text{OH})_2$, would result, and a coagulating salt, sodium sulphate or chloride, would remain in solution. Ammonium carbonate is a very effective coagulant while borax serves as a coagulant or deflocculent according to the conditions. The other chemicals used for the floating of enamels are capable of flocculat-

¹ *Trans. Am. Ceram. Soc.*, **II**, 369 (1909).

ing the clay under the proper conditions and we have every reason for assuming that this is their mode of action.¹

As pointed out by Mayer, it is theoretically a mistake to introduce a sulphate, such as magnesium sulphate, into a ground coat on account of the danger of the development of sulphur blisters. However, magnesium sulphate is the most commonly employed vehicle with the exception of clay, and apparently the small amounts added are not harmful. Greenwald recommends the addition of magnesium oxide (calcined magnesium carbonate) and ammonium carbonate as being chemically harmless.²

Magnesium oxide and carbonate, calcium oxide, calcium hydroxide (milk of lime) and calcium carbonate, may cause serious difficulties if deposited upon the ware in large granules. These granules will not be melted into the ground coat or enamel but burn to particles of quicklime (CaO or MgO). In the course of several months some of these particles will hydrate, the moisture presumably working through the porous iron with which they are in contact, and expand. This causes the enamel above them to break off in little cone-shaped spalls. This liability is not an imaginary one, for the writer has inspected ware to the value of twenty thousand dollars, in one stockroom, ruined in this manner. For this reason it is preferable to eliminate the insoluble compounds of magnesium or calcium as vehicles for floating the enamels.

The so-called "vehicles" may be added when the ground coat is charged into the mill, but the more common practice is to add the clay just previous to the grinding and to add the others to measured quantities of the ground coat just before its application. When vehicles other than clay are used, the consistency of a ground coat varies greatly with age.

The most simple and oldest type of glassy ground coat consists of a refractory frit, high in sand or flint and generally containing cobalt, to which only enough clay to float it is added at the mill. Ground coats Nos. 2 and 3 are typical formulas, showing the range of lead oxide and borax commonly employed in this type

¹ H. E. Ashley, "Technical Control of the Colloidal Matter in Clays," Bur. Standards, *Tech. Paper*, 23, 74-102.

² *Sprechsaal*, 43, 594.

of ground coat. The variations in cobalt oxide are also within the normal limits. Ground coats containing a high percentage of borax are more popular than those high in lead oxide, and formulas similar to No. 2 are in more common use than those similar to No. 3.

With the general adoption, in late years, of feldspar cover enamels, it is quite natural that feldspar should have been introduced into ground coat frits. The feldspar has not replaced flint and sand entirely as in many cover enamels—a formula for a ground coat containing neither flint nor sand being very unusual.

With the introduction of frit kilns it was not advisable to include the cobalt in the ground coat frit, as the kiln could not be used for both the white and colored enamels. Consequently, in some modern formulas we find cobalt oxide as an addition to be made at the mill. No. 4 is a typical ground coat formula containing feldspar in the frit, the cobalt being added at the mill.

It was quite natural that, from time to time, enamel mixers should attempt the blending of two ground coats. In some cases the results were so satisfactory that the use of a formula calling for the blending of two ground coats became an established factory practice. According to the results obtained by J. H. Coe,¹ in some cases the blending of two ground coats having about the same heat range will produce coats having longer heat ranges than is obtained by the use of either coat alone. No. 5 is a typical ground coat formula of this kind. Incidentally it calls for the addition of raw magnesium carbonate.

In the four glassy ground coat formulas already given, the frits themselves are quite refractory and comprise the bulk of the coat. The raw material consists essentially of only sufficient clay to float the enamel. In late years, since the rather general use of frit kilns for the smelting of ground coat frits, the use of formulas containing more fusible frits and larger amounts of refractory raw additions has been practiced in a number of plants. Formula No. 6 is typical of a number of ground coats in use

¹ *Trans. Am. Ceram. Soc.*, 13, 531-549 (1911).

which contain large amounts of clay as the raw refractory addition. One advantage of this type of formula is that the use of chemical "vehicles" for floating the coats can be avoided.

The use of clay alone as the raw refractory, in case the amount to be added is large, is not as common as the employment of a small or moderate amount of clay as a floating agent and the addition of either flint or feldspar, or both, as refractory ingredients. No. 7 is a formula of a ground coat calling for clay, flint and feldspar as the raw additions. In this formula two frits are blended, the effect being the same as the blending of two ground coats. This ground coat is more fusible than the preceding ones, being employed in the enameling of light castings.

It is somewhat difficult to estimate the comparative fusibilities of a series of enamel formulas, whether these be presented in the proportions of the raw batch, percentage composition, or empirical chemical formulas. When only one refractory ingredient is used, some idea of the fusibility may be obtained by observing the percentage of the refractory addition in the melted enamel. For this reason, in submitting the composition of cover coat enamels, we have employed formulas calling for potash feldspar as the only refractory. It is impossible to follow this practice in ground coat enamels, for the clay, flint and feldspar must be taken into consideration.

By practical trial the writer has determined that, in cast iron enamels, the potash, feldspar, flint and clay may be substituted for one another without changing the fusibility of the enamel, the ratio being 100 feldspar : $66\frac{2}{3}$ flint : 40 clay.¹ By assuming that flint is substituted in these ratios for all of the clay and feldspar contents in each of the ground coat formulas given here and by reducing the batch to 1000 pounds (melted), we obtain a number indicating the pounds of flint that would have been used for 1000 pounds of the ground coat melted, if the only refractory employed had been flint. We have called this number the "flint equivalent" of the formula. The flint equivalent of a ground coat gives a fair indication of its refractoriness, for variation in the amount of the flint added has such a decided effect

¹ *Trans. Am. Ceram. Soc.*, 13, 505 and 534 (1911).

that the influence of variations commonly found in the relative amounts of the fluxing oxides may be neglected.

Ground coat No. 1 is quite refractory and has a high "flint equivalent." Ground coat No. 7 is quite fusible and has a correspondingly low "flint equivalent." Ground coats Nos. 2 to 6 are supposed to be well adapted to general lines of enameled iron wares. It is remarkable how nearly uniform are the "flint equivalents" of these five recipes obtained from various sources.

Ground Coat No. 1.

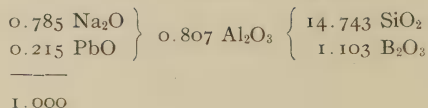
Batch for 1000 pounds.					Percentage composition.
Frit.	Raw.	Melted.			
Flint.....	350.0		SiO ₂	77.83	} 84.99
Borax.....	185.0		Al ₂ O ₃	7.16	
Sodium nitrate...	35.0		Na ₂ O.....	4.28	
Red lead.....	41.0		B ₂ O ₃	6.77	
			PtO.....	4.00	
	611.0	500.0			100.04

Additions.

Flint.....	345.0	345.0
Clay.....	180.0	155.0
	1136.0	1000.0

"Flint equivalent" = 869

EMPIRICAL CHEMICAL FORMULA.

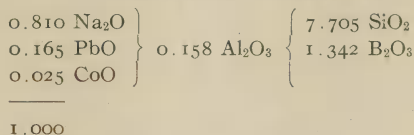


Ground Coat No. 2.

Batch for 1000 pounds.			Percentage composition.	
Frit.	Raw.	Melted.		
Flint.....	675.0		SiO ₂	70.28
Borax.....	390.0		Al ₂ O ₃	2.39
Sodium nitrate...	35.0		Na ₂ O.....	7.60
Red lead.....	52.5		B ₂ O ₃	14.27
Cobalt oxide.....	3.0		PbO.....	5.15
			CoO.....	0.30
	1155.5	948.0		99.99
Addition.				
Clay.....	60.0	52.0		
	1215.5	1000.0		

"Flint equivalent" = 736

EMPIRICAL CHEMICAL FORMULA.

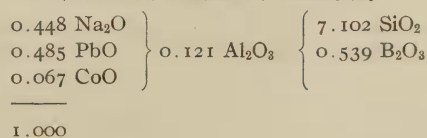


Ground Coat No. 3.

Batch for 1000 pounds.			Percentage composition.	
Frit.	Raw.	Melted.		
Flint.....	680.0		SiO ₂	70.36
Borax.....	170.0		Al ₂ O ₃	2.03
Sodium nitrate...	50.0		Na ₂ O.....	4.57
Red lead.....	170.0		B ₂ O ₃	6.26
Cobalt oxide.....	0.85		PbO.....	16.66
			CoO.....	0.085
	1070.85	956.0		99.97
Addition.				
Clay.....	51.0	44.0		
	1121.85	1000.0		

"Flint equivalent" = 735

EMPIRICAL CHEMICAL FORMULA.



Ground Coat No. 4.

Batch for 1000 pounds.			Percentage composition.	
Frit.	Raw.	Melted.		
Sand.....	275.0		SiO ₂	58.30
Potash feldspar...	435.0		Al ₂ O ₃	10.27
Borax.....	375.0		K ₂ O.....	7.35
Red lead.....	41.0		Na ₂ O.....	6.07
			B ₂ O ₃	13.72
	1126.0	948.0	PbO.....	4.00
			CoO.....	0.30
				100.01
Additions.				
Clay.....	57.0	49.0		
Cobalt oxide.....	3.0	3.0		
	1186.0	1000.0		
"Flint equivalent" = 733				

EMPIRICAL CHEMICAL FORMULA.

0.392 K ₂ O	} 0.507 Al ₂ O ₃	{ 4.884 SiO ₂	
0.493 Na ₂ O			
0.095 PbO			
0.020 CoO			
1.000			
<td>0.985 B₂O₃</td>			0.985 B ₂ O ₃

Ground Coat No. 5.

Blue ground coat. Batch for 1000 pounds.			White ground coat. Batch for 1000 pounds.		
Frit.	Raw.	Melted.	Frit.	Raw.	Melted.
Sand.....	685.0		Sand.....	395.0	
Borax.....	335.0		Potash feldspar.....	315.0	
Sodium nitrate.....	30.0		Borax.....	335.0	
Red lead.....	85.0		Sodium nitrate.....	30.0	
Cobalt.....	2.7		Red lead.....	60.0	
	1137.7	958.0		1135.0	958.0
Additions.			Additions.		
Clay.....	48.0	41.0	Clay.....	48.0	41.0
Magnesium carbonate	3.0	1.5	Magnesium carbonate	3.0	1.5
	1188.7	1000.5		1186.0	1000.5
"Flint equivalent" = 734			"Flint equivalent" = 730		

The final ground coat is made by taking two parts of blue ground coat and one part of white ground coat. This gives a flint equivalent of 733.

Percentage composition.	
SiO ₂	67.82
Al ₂ O ₃	3.80
K ₂ O.....	1.77
Na ₂ O.....	6.66
B ₂ O ₃	12.13
PbO.....	7.50
MgO.....	0.14
CoO.....	0.18
<hr/>	
100.00	

EMPIRICAL CHEMICAL FORMULA.

0.115 K ₂ O	}	0.224 Al ₂ O ₃	{	6.827 SiO ₂
0.646 Na ₂ O				
0.021 MgO				1.033 B ₂ O ₃
0.203 PbO				
0.015 CoO				

1.000

Ground Coat No. 6.

Batch for 1000 pounds.		Percentage composition.	
Frit.	Raw. Melted.		
Sand.....	200.0	SiO ₂	48.00
Feldspar.....	200.0	Al ₂ O ₃	16.61
Borax.....	390.0	K ₂ O.....	3.38
Sodium nitrate.....	30.0	Na ₂ O.....	7.42
Red lead.....	100.0	B ₂ O ₃	14.27
Magnesium carbonate...	10.0	PbO.....	9.80
		MgO.....	0.48
	930.0 720.0	CoO.....	0.10
<hr/>		<hr/>	
		100.06	

Additions.

Clay.....	325.0	279.0
Cobalt oxide.....	1.0	1.0

1256.0 1000.0

"Flint equivalent" = 732

EMPIRICAL CHEMICAL FORMULA.

0.167 K ₂ O	}	0.758 Al ₂ O ₃	{	3.72 SiO ₂
0.553 Na ₂ O				
0.056 MgO				
0.219 PbO				0.95 B ₂ O ₃
0.005 CoO				
<hr/>				
1.000				

Ground Coat No. 7.

Batch for 1000 pounds.

Frit. No. 1.	Raw.	Melted.	Percentage composition.	
Potash feldspar.....	300.0	SiO ₂	50.63	} 61.34
Borax.....	115.0	Al ₂ O ₃	10.71	
Sodium nitrate.....	20.0	K ₂ O.....	7.10	
Red lead.....	125.0	Na ₂ O.....	4.36	
	<hr/>	B ₂ O ₃	6.95	
	490.0	PbO.....	20.30	
			<hr/>	
			100.05	

Frit No. 2.

Flint.....	125.0
Borax.....	75.0
Sodium nitrate.....	15.0
Red lead.....	82.0
	<hr/>
	250.0

Additions.

Clay.....	75.0	65.0
Flint.....	75.0	75.0
Feldspar.....	120.0	120.0
	<hr/>	<hr/>

1127.0 1000.0

"Flint equivalent" = 658

EMPIRICAL CHEMICAL FORMULA.

0.31 K ₂ O	}	0.428 Al ₂ O ₃	{	3.444 SiO ₂
0.29 Na ₂ O				
0.40 PbO				0.404 B ₂ O ₃
<hr/>				
1.00				

DISCUSSION.

MR. LANDRUM: In the percentage composition given, do you include the mill mix or is it merely the batch mix?

PROF. STALEY: That is a calculated percentage composition.

MR. LANDRUM: But does it include the addition at the mill?

PROF. STALEY: Yes.

MR. LANDRUM: And does the empirical formula also include the mill addition?

PROF. STALEY: Yes.

MR. LANDRUM: Ground coat No. 7 is very similar to a sheet steel ground coat.

MR. POSTE: I have been interested in some of the work Prof. Staley has carried out in the past, relative to the possible substitution of one refractory for another and producing the same fusibility. An interesting point is that this "flint equivalent" is apparently the outgrowth of that work. I assume that the work done heretofore was derived from actual experiment and has been verified in practice. This is a much more complicated case of the same thing. Is it practicable?

PROF. STALEY: This was not tried out at all. These are formulas which were obtained from various sources. I calculated the "flint equivalent" from the factory formulas. In five formulas, supposedly used for general sanitary work, bathtubs, etc., the "flint equivalent" was about the same and we had every reason for assuming that about the same temperature is employed in most factories in maturing the ground coats. These were not made up in order to verify the "flint equivalent." I calculated the "flint equivalent" after the enamel had actually been used in the factory.

MR. POSTE: What would be the effect of replacing the feldspar and other refractory materials by the theoretical amount of flint? Have you determined this experimentally?

PROF. STALEY: Yes.

MR. POSTE: What were the results as compared to those of the previous experimental work?

PROF. STALEY: I operated a factory for four years on that basis, that is, substituting one material for another on the basis of experimentally determined equivalents.

MR. POSTE: The old question of cobalt in the ground coat is always interesting to us, and one little piece of experimental work we were conducting a while ago brought forth the very interesting proof of one theory; that under certain conditions in steel ground coats containing cobalt oxide, metallic cobalt actually separates and alloys with the steel. We happened to be doing some fundamental work, involving mixtures which included no oxidizing materials whatever, but containing cobalt oxide. After withdrawing the stirring rod from the molten batches containing no oxidizing material, there was a peculiar glossy coating on the surface of the rod. It appeared to be metallic cobalt. We sawed off the end of this rod and found that metallic cobalt had been deposited. We were endeavoring to determine the effect of nitrates and we substituted increasing amounts of nitrates for carbonates without varying the Na_2O content, and the tendency of the cobalt to deposit on the steel rod gradually disappeared, indicating that the oxidizing material kept it in the oxidized form and in the absence of an oxidizing material it was reduced, a deposit of metallic cobalt forming on the surface of the rod.

THE BONDING STRENGTHS OF A NUMBER OF CLAYS BETWEEN NORMAL TEMPERATURE AND RED HEAT.

BY C. W. SAXE AND O. S. BUCKNER.

The strength of clays at the temperatures and conditions to which they are subjected prior to and during the early stages of burning is of considerable interest, inasmuch as low strength is often a direct and always an indirect cause of the breakages which occur between the time the ware is fashioned and the time the burning operation has reached its maximum intensity.

In this connection the investigations¹ by Kerr and Montgomery have shown that much depends on the manner and the thoroughness of the drying treatment to which a clay is subjected. Thus, owing to a small amount of water retained in its pores, St. Louis fire clay, when in an air-dried condition, was found to attain not more than 50 per cent. of the strength that it possessed when drying was completed at 110° C.

Although the thoroughness of the drying treatment has a marked effect on the strength, in factory practice it is not practicable, of course, to maintain dryers at temperatures high enough to remove all hygroscopic water. Even if it were, one or more operations on the ware are usually necessary after it comes from the dryer, during which time it suffers a falling off in strength—owing to the absorption of moisture induced by room temperatures and conditions. The loss due to breakage largely depends, therefore, on the selection of clays that are strong and tough under the conditions of use.

In the most approved method of measuring the strength of clays, the drying conditions are definitely specified and are concluded with a temperature of 110° C, which is continued until

¹ *Trans. Am. Ceram. Soc.*, 15, 270, 345 (1913).

constant weight is reached.¹ However, it is known that some clays when subjected to a drying treatment possess the property of retaining moisture more tenaciously than others, and, on the other hand, of absorbing it more readily when removed from a dryer and allowed to cool at atmospheric conditions. Since the presence of small amounts of water materially reduces strength, it is probable that this affinity for water, shown in a variable degree by different clays, has an appreciable influence on the strength at conditions existing in the factory. If such be the case, then the relative strengths of a number of clays at factory conditions would be expected to be somewhat different than their order when properly and thoroughly dried at 110° C.

In investigating this matter, an attempt was made to determine: first, whether or not the strength of clay, dried in the approved manner at 110° C, is indicative of the strength of clay as it is likely to be used in the factory; second, to what extent a number of representative clays in a dry condition differ as to their affinity for moisture; and third, the relative effects of moisture on the strengths of these clays.

Another phase of this investigation is concerned with the strength of clays during the early stages of burning. While strength changes in clays in both the unburned and burned² conditions have been shown, little has been published regarding the changes in this property between 110° C and a red heat.

Tests therefore were made, first, to determine the changes in hot and cold strength from normal temperatures to red heat with particular attention to the changes undergone during the dehydration period, and second, to note if the strength of clay, thoroughly dried at a final temperature of 110° C, could be used as an index of the strength at the higher temperatures.

¹ A satisfactory drying treatment and the one used by Kerr and Montgomery is as follows:

- a. Air drying for about seven days.
- b. Drying to constant weight at 75° C.
- c. Further drying to constant weight at 110° C.

² Bleining, "Porosity and Strength of Clay Products," *Trans. Am. Ceram. Soc.*, 12, 564 (1910).

Experimental Work.

The trade names and general character of the clays used in these tests are given in Table I:

TABLE I.—CLAYS USED IN THE TESTS.¹

Name.	Mark.	
Kentucky No. 5 ball clay.....	A	Good plasticity.
Johnson-Porter No. 10 ball clay	B	Good plasticity
Armstrong clay.....	C	Very good plasticity; not refractory.
Whiteways ball clay.....	D	Good plasticity
Allen plastic clay.....	E	Good plasticity; a No. 3 fire clay.
Schippach clay.....	F	Very good plasticity; German crucible clay.
U. S. A. clay.....	G	Very good plasticity; American crucible clay.
Michigan slip clay.....	H	Poor plasticity.
Albany slip clay.....	I	Fair plasticity.
Mitchell ball clay.....	J	Very good plasticity.

For the first phase of this investigation each clay was tested for bonding strength, the tensile strength of a clay-alundum mixture being taken as a measure of this property. Each set of tensile strength briquettes was subjected to the following drying treatments:

- (1) Dried in air, at 55° C, at 110° C to constant weight and cooled in a desiccator over calcium chloride.
- (2) Air-dried at room conditions.
- (3) Dried in air, at 55° C to constant weight and then allowed to stand at room conditions for 24 hours.
- (4) Dried in air, at 55° C, at 110° C to constant weight and then allowed to stand at room conditions for 24 hours.

In the first treatment, representing the method employed for completely drying the briquettes, the second drying tempera-

¹ Chemical Analyses of the Clays:

Mark.	H ₂ O.	Loss.	SiO ₂ .	Fe ₂ O ₃ .	TiO ₂ .	Al ₂ O ₃ .	CaO.	MgO.	K ₂ O.	Na ₂ O.	Total.
A	1.29	10.03	56.56	3.32	2.00	27.52	99.43
B	0.68	10.77	51.23	2.10	1.60	34.37	100.07
C	2.32	7.49	52.34	8.77	0.80	27.87	99.59
E	1.95	10.54	57.74	2.66	1.70	23.52	0.30	1.26	0.98	0.09	98.80
F	4.00	11.94	52.01	3.11	0.75	31.99	99.80
H	4.42	6.33	60.66	2.83	1.12	12.28	7.77	2.55	...	5.27	98.23
I	1.21	7.69	55.73	4.94	1.02	15.97	5.51	3.17	99.63

ture, 55°C was used, but as the briquettes were largely composed of non-plastic material, this was found to give satisfactory results. The remaining treatments approximate the average and extreme conditions likely to prevail in the factory.

In addition to the briquettes, trial peices of each clay were prepared and dried at the same time as the briquettes. The water contents were then determined by drying to constant weight at 110°C .

The results of this work are given in Tables 2 and 3 and Figs. 1 and 2.

The strengths of the clays between normal temperatures and red heat were determined on both hot and cold briquettes and at such temperatures as to include the dehydration period. In order to observe the commencement and duration of this period, loss of weight determinations and dehydration lag curves were made for each clay. Porosity determinations were also carried out per chance such data might be correlated with the bonding strengths. The results of these tests are given in Tables 4, 5, and 6, and are presented graphically in Figs. 3 to 13, inclusive.

Methods of Testing.

The Briquettes.—All of the briquettes were made from mixtures of 25 per cent. 46-mesh clay and 75 per cent. No. 60 "regular alundum" and molded into standard cement briquettes while in a soft plastic condition. Before testing, the faces of the briquettes were rubbed parallel and one end made flat in order to facilitate handling in the electric oven.

Drying Treatments.—The drying treatments for the first part of this study were carried out as prescribed under "Experimental Work." Each operation at 55°C and 110°C was continued till practically constant weight was reached.

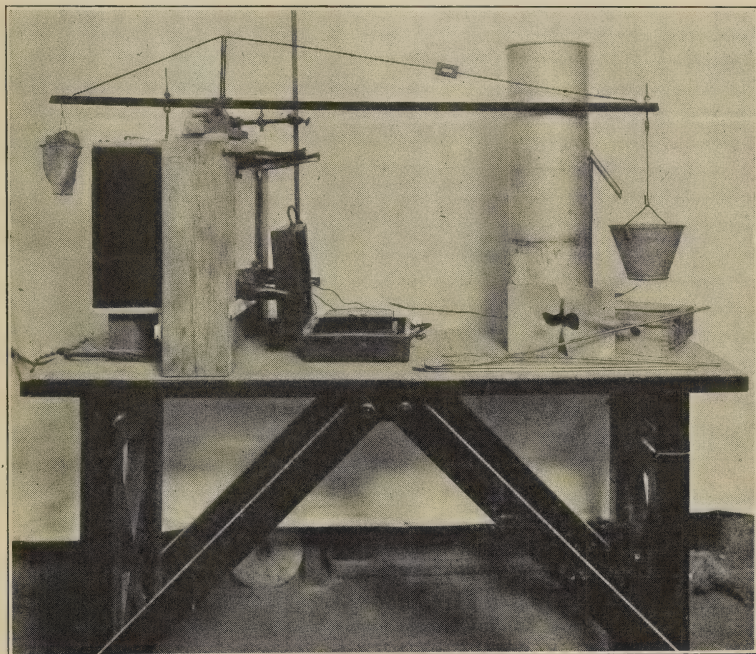
Heat Treatments.—In the tests to determine the changes in strength during the early period of burning, the briquettes that were tested while hot at 200°C and above were held at the desired temperature for one hour before breaking, these temperatures being reached at the rate of 2.3°C per minute. Those that were broken cold were first partly cooled in the furnace itself and

then removed to a desiccator. Heat treatments below 200°C , however, were somewhat different in that they were continued until the briquettes were constant in weight.

A Hoskins electric furnace was used for the treatments above 110°C , the temperature being measured up to 325°C by means of a mercurial thermometer and above this point by means of a thermocouple.

Bonding Strength.—The testing machine used was a simple device and consisted chiefly of a lever of the first class fitted with a pair of clips or holders. The load was applied at the rate of 50 pounds per minute.

For breaking the briquettes in a hot condition, special refractory clips were prepared and connected with the arm of the lever through a small hole in the top of the Hoskins furnace. This apparatus is shown in the illustration.



Apparatus for breaking the hot briquettes.

Six briquettes were thought sufficient to provide a good average result for the drying treatments at and below 110°C . For the higher heat treatments this number was reduced to four and in a few cases three.

Loss in Weight.—The trial pieces used for this test were $\frac{3}{8}'' \times \frac{3}{4}'' \times 4''$ in size and were cut from a slip-made slab of clay when in a leather hard condition. Raw, dry weights were obtained after a final drying treatment at 110°C to constant weight. Each test piece was held for one hour at the desired temperature, using the same rate of heating as employed for the briquettes. When necessary, the bars were partly cooled in the furnace and then removed to a desiccator. The per cent. loss in weight is expressed in terms of the dry weights as obtained at 110°C .

Porosity was determined on the same pieces that were used for loss of weight, by Purdy's formula,¹

$$\frac{(W - D)}{(W - S)} \times 100 = \text{per cent. porosity,}$$

where

W = Saturated weight,

D = Dry weight,

S = Saturated suspended weight.

(The saturating liquid was kerosene.)

Dehydration Lag Curves.—The dehydration curves were obtained by inserting a thermocouple into the center of a specimen of clay $\frac{3}{4}'' \times \frac{3}{4}'' \times 1\frac{1}{4}''$ in size which was then heated at the rate of about 24°C per minute in an electric furnace having a chamber 2" in diameter by $2\frac{5}{8}''$ deep. Temperature readings were taken every 15 seconds. No rheostat was placed in series with the furnace. The heating curve was obtained by using an already dehydrated specimen.

Results.

The calculated data given in Table 3 expresses the per cent. loss in strength that each clay has undergone on the absorption

¹ Illinois Geological Survey, *Bull.* 9, 142.

of moisture, the latter being expressed in terms of the water required by each clay to bring it to normal plasticity.

Discussion of Results.

Bonding Strengths of the Clays. Relative Order of Strengths at Factory Conditions and When Completely Dried at a Final Temperature of 110°C . Table 2, Fig. 1.—The bonding strengths of the clays when completely dried at a final temperature of 110°C are only roughly indicative of the strengths at factory conditions. Not only is strength materially decreased by the presence or further absorption of moisture but the relative order of the clays, particularly the stronger ones, is changed. Thus, clay J, which has a bonding strength of 130 pounds per square inch when completely dried at a final temperature of 110°C , falls among the class of mediocre clays when allowed to stand at room conditions for 24 hours. On the other hand, clay F, having a strength of only 88 pounds, is among the strongest at factory conditions. Clays C and G are further examples; when dried to constant weight at a final temperature of 110°

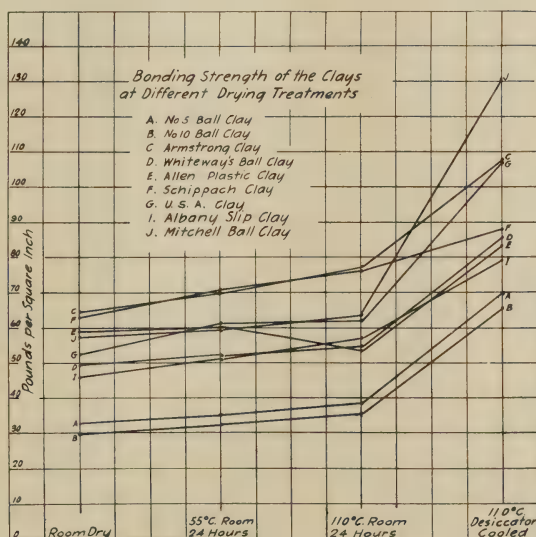


FIG. 1.

TABLE 2.—BONDING STRENGTH IN POUNDS PER SQUARE INCH OF THE CLAYS AFTER THE DIFFERENT DRYING TREATMENTS.

Clay.	Air dried.	Dried at 55° C. Room 24 hours.	Dried at 110° C. Room 24 hours.	Dried at 110° C. Desiccator cooled.
A.....	32.9	34.9	38.7	69.8
B.....	30.1	32.5	35.4	65.8
C.....	65.3	69.9	77.1	107.4
D.....	49.7	52.1	54.5	85.5
E.....	58.9	59.8	54.4	83.3
F.....	64.1	70.6	76.1	87.9
G.....	52.6	61.2	62.0	107.2
I.....	46.1	51.2	57.3	79.2
J.....	57.5	59.4	63.4	130.5

TABLE 3.—PER CENT. LOSS OF STRENGTH PER PER CENT. MOISTURE CONTENT EXPRESSED IN TERMS OF THE WATER OF PLASTICITY.

Drying Treatment No. 4 at 110° C, Room 24 Hours.

Clay.	Per cent. loss in strength.	Per cent. water content.	Water of plasticity.	Ratio of the per cent. water content to the water of plasticity.	Ratio of the per cent. loss in strength to the ratio of the per cent. water content and the water of plasticity.
A.....	44.5	0.98	36.5	2.68	16.6
B.....	45.5	0.98	34.0	2.88	15.8
C.....	28.2	1.64	34.0	4.82	5.9
D.....	36.3	0.93	35.9	2.59	14.0
E.....	34.7	0.95	33.5	2.83	12.3
F.....	13.4	2.00	33.8	5.92	2.3
G.....	42.1	1.21	35.4	3.42	12.3
I.....	27.6	0.55	22.2	2.48	11.1
J.....	51.4	1.24	39.2	3.16	16.2

Drying Treatment No. 3 Dried at 55° C, Room 24 Hours.

A.....	50.0	1.13	36.5	3.09	16.2
B.....	50.6	1.13	34.0	3.32	15.2
C.....	34.9	2.02	34.0	5.94	5.9
D.....	39.0	1.33	35.9	3.70	10.5
E.....	28.2	1.22	33.5	3.64	7.8
F.....	19.7	2.89	33.8	8.55	2.3
G.....	42.9	1.79	35.4	5.07	8.5
I.....	35.3	0.63	22.2	2.84	12.4
J.....	54.5	1.95	39.2	4.97	10.9

they are practically identical but vary noticeably at the other drying treatments.

Affinity for Water and Its Relative Effect. Table 3, Fig. 2.—The data given in Table 3 show that there is considerable variation in the water content of the clays after the same drying treatments. For instance, clay F absorbed from three to four times as much moisture as clay I when dried at a final temperature of 110°C and allowed to stand at room conditions for 24 hours.

The different clays, however, are very dissimilarly affected by this moisture. For instance, clay J (Table 3), though it absorbed less moisture than clay F, suffered a much greater loss of strength. If the per cent. loss in strength per per cent. moisture content is calculated for each clay it will be found to vary from approxi-

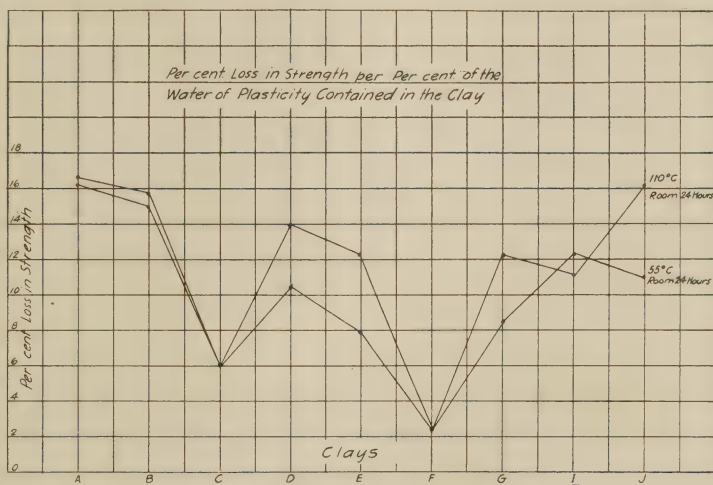


FIG. 2.

mately 7 to over 50 per cent. This great diversity in loss of strength for equal amounts of water is still further shown by Fig. 2. The results therein presented express the per cent. loss in strength per unit amount of water of plasticity which each clay retained or absorbed at two of the drying treatments. The clays vary considerably—the smallest loss per unit amount of

water being approximately two per cent. and the largest over 16 per cent.

This greater susceptibility on the part of some clays to the effects of moisture seems to be the chief cause for the dissimilarity of the relative order of the bonding strengths after the different drying treatments.

Strength of the Briquettes Broken while Cold between Normal Temperatures and Red Heat. Table 4, Figs. 3 to 13, Inclusive.— Aside from the increase in strength between normal temperatures and 110°C , all of the clays show but small changes in strength up to 325°C . Above this temperature, and during the dehydration period, all increase in strength quite rapidly with the exception of the two slip clays, which remain practically constant until red heat is reached.

Strength of the Briquettes Broken while Hot between Normal Temperatures and Red Heat. Table 4, Figs. 3 to 13, Inclusive.— In all cases the strength of the briquettes when broken while hot is lower than the strength of the briquettes similarly treated but broken while cold up to and through the dehydration period.

Starting at 55°C , clay B shows the greatest loss in strength and clay G the least, the former having decreased 20 per cent. and the latter approximately 2.0 per cent. The average difference for all the clays is 10 per cent.

At 110°C none of the clays show the characteristic increase in strength that is evident in every case when broken cold. In fact, the tendency seems to be to decrease slightly below that at 55°C . The average loss of all the clays at this point compared to the average cold strength at 110°C is 28 per cent.

The majority of the clays at 200°C show a further slight decrease, but at 325°C a slight increase is evident in most cases. Above this temperature and through the dehydration period strength continues to gain rapidly. The one exception is Michigan slip clay which remains practically constant up to 700°C .

Generally speaking, the clays that have the highest cold strength at 550°C are also the strongest in the hot condition during the

TABLE 4.—BONDING STRENGTH OF THE CLAYS BETWEEN NORMAL TEMPERATURES AND RED HEAT.

		Cold—desiccator cooled.						Hot.							
Clay.	Room dry 20° C.	55°.	110°.	200°.	325°.	575°.	825°.	55°.	110°.	200°.	325°.	450°.	575°.	700°.	825°.
A	38	60	62	76	84	126	163	49	52	53	53	65	93	134	171
B	36	59	66	73	78	129	158	47	49	57	62	74	102	165	175
C	89	114	134	129	133	151	468	98	98	89	107	119	132	172	194
D	61	80	94	98	103	151	266	74	73	61	60	80	124	135	150
E	85	107	125	121	119	184	322	94	96	84	84	112	154	189	237
F	86	91	114	127	141	253	331	88	84	71	87	122	188	221	301
G	73	104	145	145	153	255	294	102	88	101	122	148	223	274	345
H	14	19	24	17	19	9	24	17	15	14	14	14	13	13	44
I	57	75	88	80	87	92	274	70	66	58	63	74	83	109	139
J	61	89	125	110	111	195	221	75	73	73	83	97	225	226	331

TABLE 5.—PER CENT. POROSITIES AFTER THE DIFFERENT HEAT TREATMENTS.

Clay.	110° C.	200°.	325°.	410°.	450°.	575°.	700°.	825°.
A.....	34.9	36.6	37.4	37.7	37.0	39.6	39.9	40.6
B.....	37.4	39.6	40.3	40.7	39.3	41.7	42.3	43.8
C.....	34.0	36.4	38.3	38.0	37.4	38.5	38.9	39.0
D.....	33.6	35.9	38.1	38.9	37.6	40.8	41.5	42.4
E.....	33.7	34.2	37.7	38.5	37.4	40.3	41.2	41.6
F.....	28.6	30.0	31.0	28.2	30.4	33.1	33.2	33.0
G.....	34.8	36.0	36.6	36.9	36.3	38.6	39.2	39.4
H.....	40.3	44.2	44.7	43.0	43.1	44.9	48.1	47.4
I.....	35.8	37.8	37.9	38.8	37.5	39.6	42.7	41.8
J.....	32.4	31.7	32.3	32.4	31.5	34.4	34.0	35.2

TABLE 6.—PER CENT. LOSS IN WEIGHT AT THE DIFFERENT HEAT TREATMENTS.

Clay.	200° C.	325°.	410°.	450°.	575°.	700°.	825°.
A.....	0.16	0.76	0.85	1.13	7.90	8.09	8.69
B.....	0.11	0.80	0.66	1.32	9.36	9.55	10.53
C.....	0.39	1.65	1.40	2.14	5.41	5.80	7.19
D.....	0.34	2.28	2.78	3.53	9.49	9.53	10.90
E.....	0.52	3.24	3.43	4.55	8.72	9.03	9.84
F.....	1.19	1.92	0.49	2.45	9.46	9.74	11.20
G.....	0.29	1.10	1.12	1.86	10.05	10.61	11.60
H.....	0.25	0.28	0.36	0.63	2.74	7.14	7.55
I.....	0.09	0.35	0.33	0.81	3.05	7.09	7.59
J.....	0.36	0.97	0.83	1.16	8.18	8.23	9.48

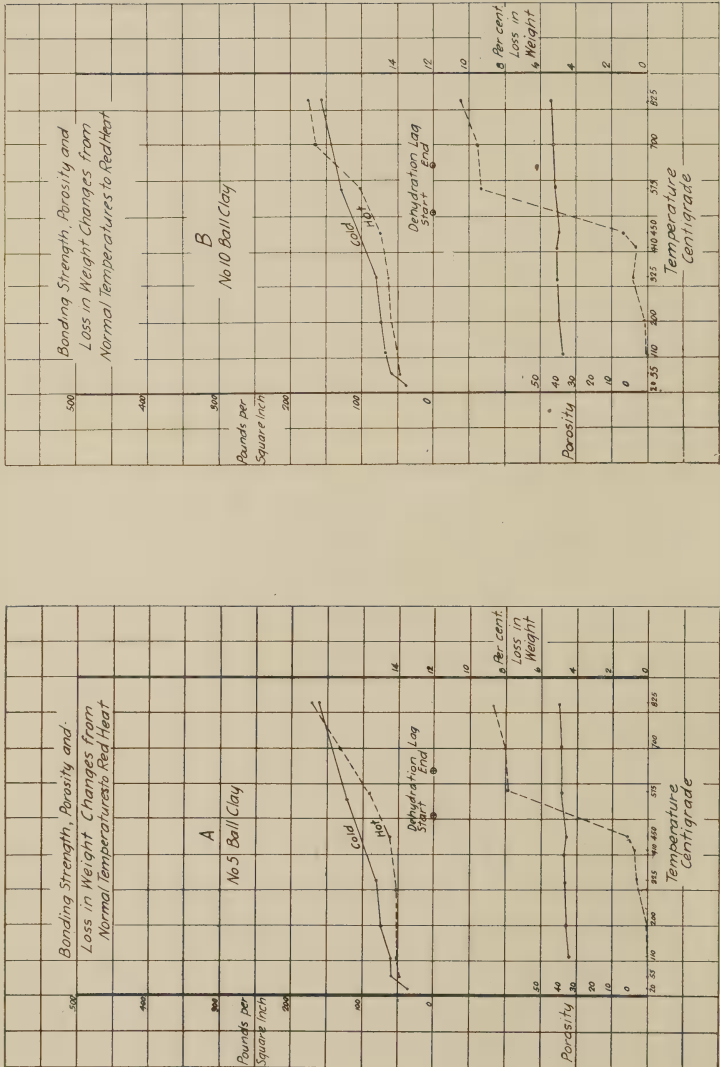


FIG. 3.

FIG. 4.

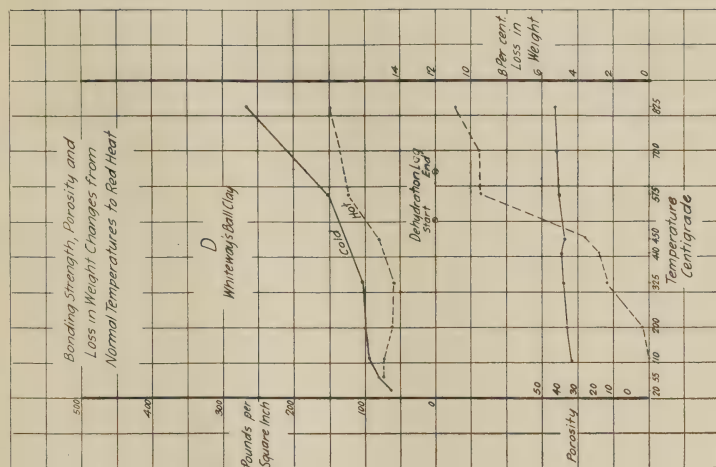


FIG. 6.

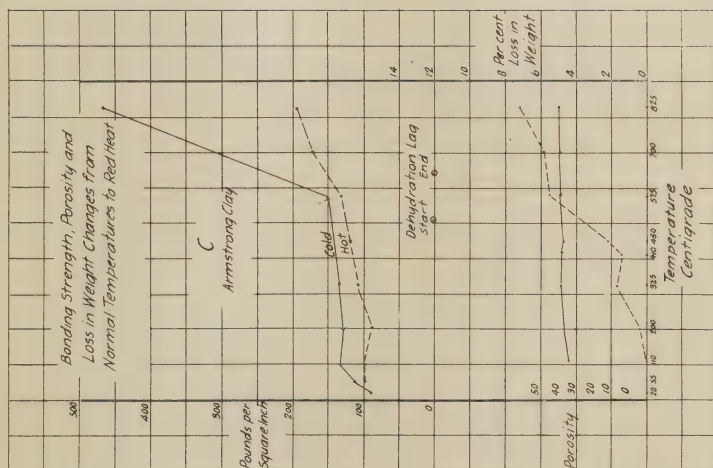


FIG. 5.

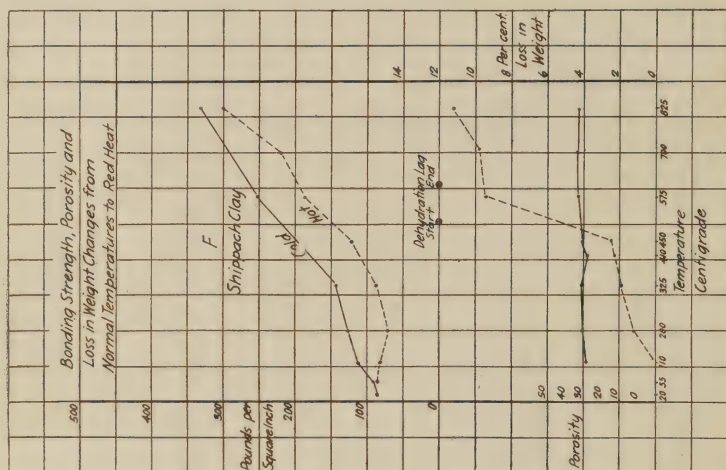


FIG. 8.

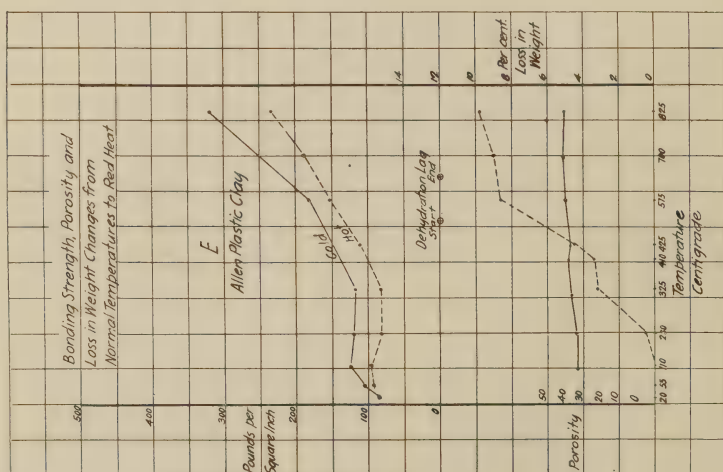


FIG. 7.

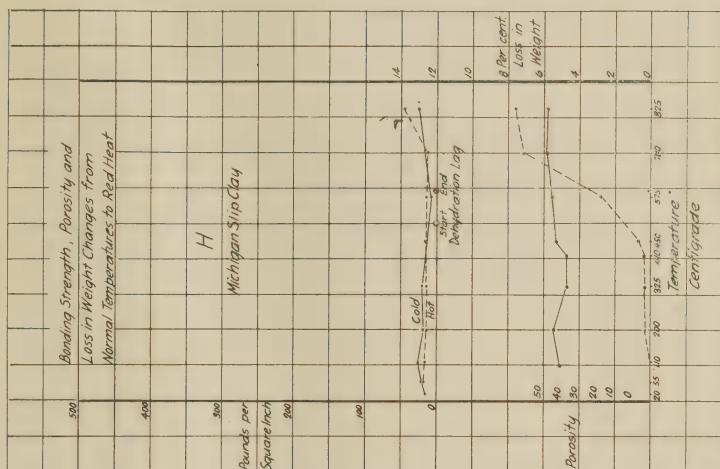


FIG. 10.

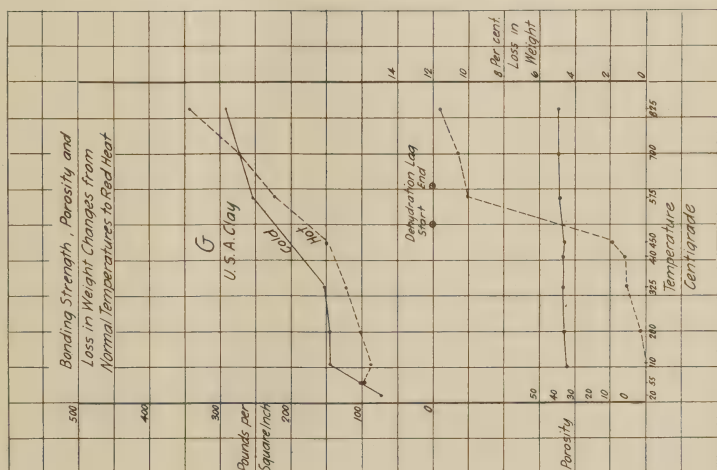


FIG. 9.

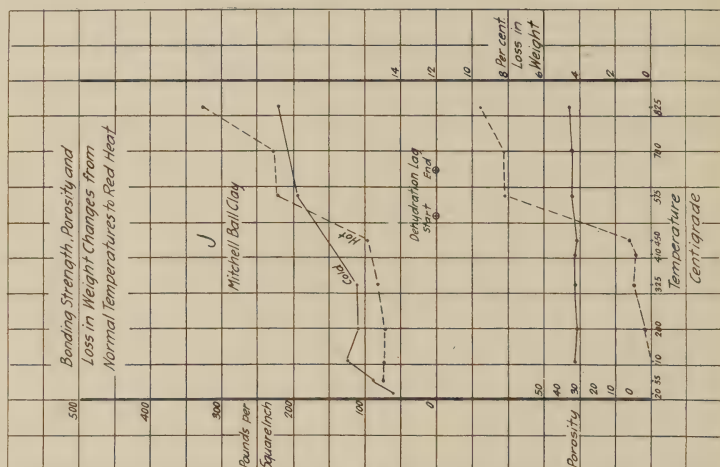


FIG. 12.

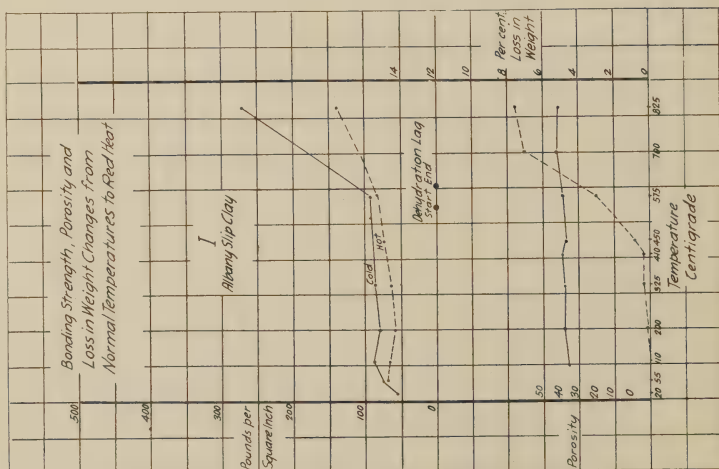


FIG. 11.

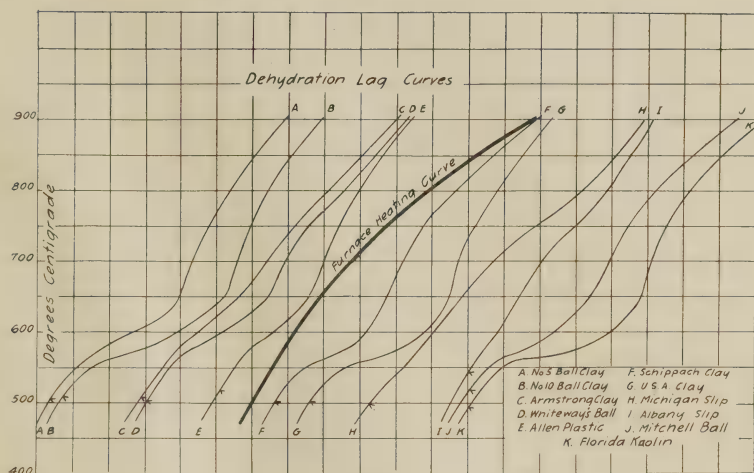


FIG. 13.

interval between 55°C and 325°C , where strength is quite low. When broken cold at the 110°C heat treatment they are less indicative of strength during this interval.

Porosity and Loss in Weight. Tables 5 and 6, Figs. 3 to 13, Inclusive.—No relation is noticeable between bonding strength and the loss in weight of the clays at the different heat treatments; this property remains constant, increases or decreases as the test pieces lose weight depending on the clay.

Likewise no relation is evident between porosity and strength for the former increases gradually at all temperatures except at or just before dehydration, where, in every case, a slight decrease takes place.

Dehydration Lag Curves, Fig. 13.—The beginning of dehydration was assumed to be at the point where the curve first departed from the normal furnace curve and the completion at the point where it first started to return. In every case the duration of this period is somewhat briefer and not in very close agreement with that indicated by the loss in weight determinations. This apparent discrepancy appears to be due to the errors attending the former method. Thus the absorption of heat, which ex-

tended in a number of cases beyond the upper limiting temperature set by the loss in weight determinations, seems to have been caused by the large size of the test specimens and the consequent inability of the small electric furnace to regain its normal rate of heating, following the endothermic reaction. The lag curves for the two slip clays agree more closely with their loss in weight determinations substantiating this view—for these clays are the most impure of the lot and lose weight over a greater interval of temperature.

Conclusions.

The strength of a clay, dried to constant weight at a final temperature of 110°C , is only a rough measure of its strength at conditions which prevail in most factories. Results thus obtained permit the selection of strong clays from weak clays but do not afford a means of distinction between, say, a number of fairly strong clays at conditions under which they are likely to be used.

When different clays are not thoroughly dried or are subjected to atmospheric conditions where the absorption of moisture is possible they show a large dissimilarity in their affinity for water. The fact that the relative order of the strengths of clays at factory conditions is appreciably different from their order when dried to constant weight at a final temperature of 110°C is partly due to this phenomenon. However, the largest and most dissimilar changes are due to the fact that the presence of small amounts of water causes some clays to lose much more strength than others.

The strength of clays in a hot condition between 110°C and red heat is considerably lower for the first two or three hundred degrees than their cold strength when thoroughly dried at a final temperature of 110°C .

During dehydration, both the hot and cold strength of clays increases or remains practically constant indicating that the physical and chemical changes during this period have little effect on this property.

Generally speaking, the strongest clays in the cold condition as dried at 55°C are in turn the strongest when hot during the interval of lowest strength between 110° and 325°C and hence

the former can be taken as a rough measure of strength during this interval.

COMMUNICATED DISCUSSIONS.

C. E. FULTON: This paper is very interesting throughout, but the most important point which has been duly emphasized by the authors is the fact that results obtained by tests upon thoroughly dried briquettes (that is, dried at 110°C and cooled in a desiccator) will give results which will not be obtained under practical conditions. It has been our practice, in testing the bonding strength of raw clays, to air-dry the test bars for one week, then place them in the drying oven at 75°C , and finally at 110°C until constant in weight. After this drying treatment the bars are taken from the oven and, when cooled to room temperature, are broken in a transverse testing machine. This method has given very consistent results and it will be interesting to know whether or not the authors have any results obtained by the breaking, as soon as they become cool, of briquettes which have been dried at 110°C .

With the exception of clay E, the results obtained with their second drying treatment (55°C , in room 24 hrs.) and third drying treatment (110°C , in room 24 hrs.) give equally good classification. The clays are grouped in pairs, F and C showing the highest strength, G and J forming the next pair, followed by D and I, and finally A and B, which show the lowest strength. The second testing method groups clay E with G and J while the third drying treatment places it with D and I. As this is the only clay which shows a falling off in strength between these two methods, it is possible that the number of pieces averaged to obtain this result (six) were too few to give it its proper position. In all strength tests from ten to fifteen briquettes should be broken to obtain a fair average.

It would add to the value of the paper if data were given showing the maximum variation from the average given for each clay, and also a record of the room conditions during the 24-hour drying period. This is one objection to the method proposed by the

authors as the room conditions introduce a variable which may make it impossible to compare results obtained at different periods and in different places.

M. F. BEECHER: It is apparent that the drying methods followed by the authors have not been made entirely clear. In Table 2, the four columns represent values obtained as described in the text under "Experimental Work."

The data presented in this paper confirm Mr. Fulton's statement that an intermediate drying temperature between room temperature and 110° C. is required to give the best results. In the present case, that intermediate temperature was 55° C. The authors have no data to present on briquettes dried directly at 110° C.

While in general practice it is agreed that at least ten briquettes should be used to obtain an average, the large amount of work of this nature which we have done has resulted in a method which has been demonstrated to give very reliable figures even though only six briquettes are used. The briquette mixtures contain only 25 per cent of clay instead of 50 per cent as ordinarily used, and granular, non-plastic of No. 60 mesh instead of No. 20 mesh. This allows of more uniformity in the molding of the briquettes and less danger of injury to the clay bond by checking in drying. The machine and method of breaking, described in the paper, contribute further to uniformity of results.

Some data on the accuracy of this method, compiled last year for the use of the Committee on Standards of the American Ceramic Society, show that in the test of 67 clays, only four show an average deviation, from the mean tensile strength of the six briquettes, of more than 7 per cent and that the grand average of these values for "average deviation from the mean" was only 4.3 per cent. Reference to the work of Bleining and Howat,¹ shows a similar value for the tension method to be 6.1 per cent. and the best result by any method was secured by the transverse test where the corresponding grand average of deviations from the mean was 5.5 per cent.

¹ *Trans. Am. Ceram. Soc.*, 16, 273 (1914).

Clay E, dried by the second and third methods described, shows the following variations in the tension test:

	Max. Deviation from Mean. Per cent.	Min. Deviation from Mean. Per cent.	Average Deviation from Mean. Per cent.
Method 2	9.0	1.5	5.3
Method 3	11.5	2.0	6.5

It was not the intention of the authors of this paper to propose a new scheme for drying briquettes for bonding strength tests. Their object was to secure the necessary data for properly interpreting laboratory results on the strength of clays into usable factory information, and to point out that the difference between laboratory and factory drying methods is such a great factor in the drying of clays, that due consideration should always be given this point in the application of laboratory values.

Incidentally, their data confirm the accuracy and reliability of the generally approved method of drying in the making of the strength tests, to which Mr. Fulton refers.

NORTON CO.,
WORCESTER, MASS.

OBSERVATIONS ON THE FORMATION OF SEED IN OPTICAL GLASS MELTS.¹

By A. E. WILLIAMS, Pittsburgh, Pa.

In a number of optical glass melts, made at the Bureau of Standard glass plant, considerable trouble was experienced from seedy glass. In practically all cases the seeds formed were quite large, varying from $\frac{1}{32}$ " to 1" in diameter, with a very few minute seeds grouped about the outer edge of the areas in which the larger seed were located.

No difficulty was experienced in the fineing of this glass, so far as could be determined, the bubbles being completely eliminated during the melting process and the glass remaining free from bubbles during the working, so long as the temperature remained above a certain minimum. These bubbles appear chiefly in our crown and boro-silicate glasses, but have occurred to some extent in the barium glasses.

In some of the melts the bubbles have been formed in a layer on the bottom, affording a cave-like appearance to the bottom 4 inches of the glass in the pot; in other cases the bubbles extended as a cone from the bottom, or the slowest cooled portion of the pot, towards the center of the glass. In one case, the seed formed in the center of the glass in the pot, the remainder of the glass being free from bubbles.

The evidence which we have been able to gather in determining the cause of this seed formation may be summed up as follows:

First, If the stirring of the glass were carried on below a certain temperature, bubbles would appear and increase in number as the stirring was continued.

Second, If the stirring were discontinued at a temperature above this minimum, and the pot were cooled without rapidly chilling the bottom, a layer of seed, having a cone shape area

¹ By permission of the Director, Bureau of Standards.

extending upwards from 5 to 10 inches in the glass, would occur on the bottom.

Third, If one end of the pot were raised off the bottom of the furnace during cooling, seed would appear in that portion of the glass which was over the part of the pot still in contact with the bottom of the furnace.

Fourth, If the cooling were started at a temperature above that at which the seed apparently first appeared during the stirring and the glass in the pot was chilled rapidly, no seed appeared.

Fifth, The contents of the bubbles in samples of this glass were analyzed by Dr. Hillebrand, of the Bureau of Standards, for CO_2 and small amounts were found present.

Sixth, Pots of these glasses which were not agitated but simply melted and fined in the usual manner until samples of the glass were free from seed, did not show any bubbles when cold. On the other hand, there have been cases known in which pots of soda lime glass, chilled by placing in the open, became full of large bubbles—this being contrary to the experience we have had with the crown and boro-silicate glasses.

It therefore seems very evident, from the above observations, that gases are evolved during the cooling of the glass at temperatures at which the glass has still quite a low viscosity, the temperature being below 1200°C . Slow cooling between 1200°C . and 700°C . increases the amount and size of these seed and rapid chilling prevents their formation.

In any case, we must recognize the fact that the formation of seed in optical glass is not necessarily due to any difficulty in the fining process, but, in many cases, it is due to some other phenomena taking place during the cooling. The gas may either be a dissociation product or may be evolved from a supersaturated solution. Like phenomena occur in the cooling of steel ingots and some of the silicates, such as diopside. However, the evolution of gas in these cases is accompanied by crystallization and the gas is probably evolved because of a decrease in solubility. It is improbable, however, that a decrease in solubility will take place upon the cooling of an amorphous glass melt, especially if Henry's Law applies to viscous liquids at high temperatures,

as it does to dilute solutions, and the gas is most probably a dissociation product. The nature of this dissociation product has not been determined but as all of these glasses contain barium, the possibility of the formation of BaO_2 , which will dissociate to BaO upon cooling, has been suggested.

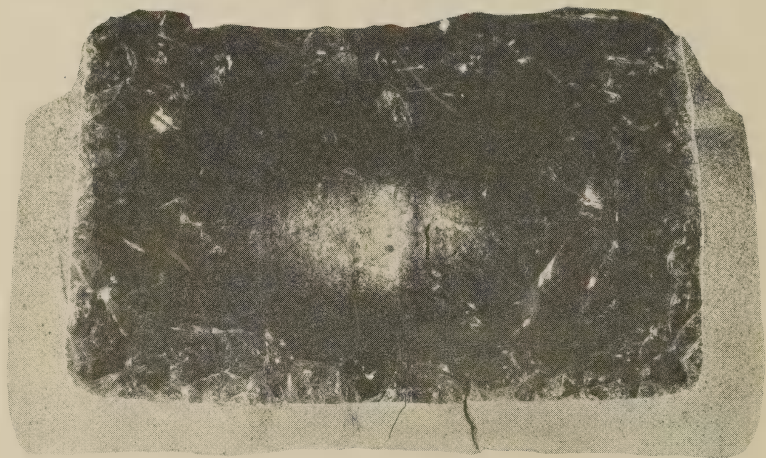


FIG. 1.—Section of a pot of dense barium optical glass showing a mass of bubbles in the center.

The accompanying illustration, Fig. 1, is of a pot of dense barium glass which was cooled from 1100°C to 600°C in five hours, the glass surrounding the light spot in the center being free from gas bubbles and the light spot being a foam-like mass of gas bubbles. This pot was cooled most rapidly from the top, bottom and sides, the center having cooled more slowly.

DISCUSSION.

MR. GATES: I would like to ask Mr. Williams if he has considered the possibility of a gas being introduced from the bottom of the pot, causing the bubbles? I have seen cases of blistering in a glaze evidenced by a similar effusion of gases, which evidently came from the body of the ware, and, in cooling, formed in the glaze. Could this gas, to which you refer, be derived from the bottom of the glass pot during the cooling, as occurs in the case of the blistering to which I referred?

MR. WILLIAMS? We at first thought that there might possibly be some evolution of gases from the bottom of the glass pot, but we have noted the formation of the gases in portions of the glass which were not closely in contact with the bottom of the pot.

MR. FRINK: I would like to ask if these pots are glazed previous to being used?

MR. WILLIAMS: The pots were glazed in the bottom only—by melting 100 pounds of cullet in the pot, previous to introducing the glass batch.

MR. FRINK: That being the case, it occurs to me that the question which you have raised as to the increased solubility of gases in the pot itself, at its higher temperatures, would account for this condition. Perhaps the zone condition of the bubbles is also accounted for by the increased or diminished porosity of the pot or the solubility of the gases in those particular zones in the pot. If that is the case, when the pot is turned up on its side, as we have often found to be the case, and is cooled on that side particularly, you will then have squeezed your gas, coming up through the hotter portions of the pot, underneath your glass until it collects. The glaze, on the bottom of the pot, being more viscous on account of its higher content of alumina, allows the gas bubbles to collect until they become enlarged. In making colored glasses, the pot is first filled and then, for some reason, the pot is cooled and taken out; you will find varying conditions in the size of these gas bubbles. The nature of the gas depends largely upon what the conditions have been and to what period of melting the batch has been subjected.

MR. WILLIAMS: I wish to state that our theory for the formation of the gas in the hotter end of the pot, when tipped up, was that the slower cooling had taken place there, giving the gas a chance for evolution. The gases were always evolved while the viscosity of the glass was reasonably low and during the interval over which the slow cooling had taken place.

MR. FRINK: You do think though, Mr. Williams, do you not, that in view of the fact that the bubbles usually occur first

near the clay surface, there is a possibility of these other gases being evolved from the pot itself and squeezed out and driven into the glass?

MR. WILLIAMS: I do not believe I do, because of the pressure. It would appear that any gas that was held in the clay pot might be expelled from the outside of the pot rather than from the inside. Another consideration would be the cooling down during that period. If the gas were mechanically included, simply present as gas in bubbles and held mechanically at the operating pressure, there would be no expansion of the gases coming from the pot walls.

MR. FRINK: True, but I was proceeding upon the theory you have advanced, that the bottom of your pot, when first raised, is very hot, the central zone of the pot bottom being much colder. The central zone of the bottom that is in contact with the bench, must, if there is any difference, be the colder portion because it is furthest removed from the source of heat. When the pot is raised on its edge and the bottom cooled, the glass next to the bottom on the inside is hotter than the portion that is cooled on the outside; therefore, if there is a squeezing out, figuratively speaking, of these gases, the gas must pass to the inside, the pot being denser on the outside on account of the cooling.

MR. WILLIAMS: I see your point, but our practice is to chill the bottom with compressed air and by so doing, we do not have this condition. We operate in this way believing that by so doing the glass is cooled too quickly to allow the gases to come out of solution. Gas bubbles do not appear when the pot is raised and quickly chilled. The bubbles are developed when the pot is allowed to set flat on the bench, the bottom remaining hot for a longer time than the other portions of the pot.

COMMUNICATED DISCUSSIONS.

F. GELSTHARP: This is a very interesting subject to a glass maker, as the presence of seed and bubbles in the product is one of his many troubles.

Bubbles of the large size to which Mr. Williams refers are never found in glass except when the glass pots are allowed to cool

down without special care being taken to prevent their formation. My experience agrees with that of Mr. Williams in that these large bubbles are located in that portion of the metal which is cooled most slowly. I have found that if the top surface of the metal is kept warm and the bottom and sides are cooled quickly, these large bubbles do not appear.

I have examined these larger bubbles and in some glasses have found them to contain sulphur dioxide and carbon dioxide, and in others only carbon dioxide, but under very reduced pressure, so low in fact, that, when punctured under water they fill completely, showing that the volume of gas is exceedingly small. This would indicate that the bubbles originated from a very small quantity of gas which has greatly expanded, owing to the surrounding conditions of greatly reduced pressure. To have this condition we must imagine the containing walls of glass to be at a temperature of rigidity, that is the sides and the top surface of the metal. As cooling of the whole mass progresses a condition of greatly reduced pressure will be produced in that portion of the glass which is still mobile; this is generally near the center and towards the bottom. Any small seed which may be in this locality will be expanded to a size depending upon the viscosity of the glass at that point.

I am of the opinion that some of our optical glasses will evolve dissolved or combined gases between certain temperatures, but in a case of this kind the liberation of gas will be throughout the whole mass, and the gas bubbles will not be very large in any particular portion of the pot, unless we have a condition of reduced pressure as described above.

I have seen old plate glass pots set out which had 9 to 12 inches of glass left in them and large bubbles of gas could be seen exuding from certain spots, which were apparently cavities in the bottom of the pot. These bubbles would stay attached to the bottom for a considerable time till they were large enough to overcome the viscosity of the glass and rise towards the surface, but generally they were arrested before reaching the surface.

It seems to me that the bubbles found by Mr. Williams when the stirring of the glass was continued too long, may have been due to the release of these bubbles exuding from the pot bottom—

the metal not being sufficiently fluid to allow them to come to the surface.

E. W. WASHBURN: Our experiments at Illinois have shown that pieces of perfectly clear glass entirely free from bubbles contain considerable quantities of gas in solution. If a clear piece of glass is heated until it softens and is then placed in a vacuum the dissolved gases are evolved in such quantities as to cause the mass of glass to swell up to several times its original size and to assume the appearance of soap suds. Owing to the viscosity of melted glass it is not impossible that certain portions of a pot of glass may be supersaturated with respect to the equilibrium between the dissolved gases and large bubbles of these gases. It is certainly true that all glass contains at least that amount of dissolved gas which corresponds to complete saturation at the maximum temperature attained during the process of fineing. A slight decrease of pressure at any time after cooling is started would be sufficient to start the evolution of this gas. Such a decrease in pressure might be brought about, for example, by a variation of the firing conditions in the furnace or by a fall in the barometer. Slow cooling would, of course, give a greater time for this result to occur, while rapid cooling would tend to prevent it both by decreasing the time during which it was possible for such a fall in pressure to take place and by increasing the viscosity to such a point that no growth of bubbles was possible.

C. W. KEUFFEL: The phenomenon described by Mr. Williams was observed in some of our melts, *i. e.*, a cone of bubbles was found to extend from the bottom of the pot toward the center. This has happened to several meltings of Boro-silicate Crown but never to a flint glass.

In each case we attributed this result to the rapid cooling of the top and sides of the pot and the relatively slow cooling of the bottom. When the pot was allowed to cool either rapidly or slowly but uniformly from the sides, top and bottom no bubbles were formed.

Our Boro-silicate Crown contains no Barium so that the suggestion that the gas in the bubbles is a dissociation of BaO_2 into BaO seems in error.

AMERICAN CERAMIC SOCIETY

Summer Meeting.

ZANESVILLE, OHIO, June 25-28, 1918.

The meeting was an exceptional one in many ways and in point of average attendance it materially surpassed that of the former summer meetings. More than 90 were enrolled, seventy-five of those in attendance having come from a distance.

Tuesday, June 25th:

In the morning the members assembled at the Hotel Rogge, Zanesville, and after registration, proceeded to the plant of the Mosaic Tile Company. The Dressler Tunnel kilns in operation at this plant were inspected, one being used in the bisque firing and the other in the glost firing. Another interesting feature at this plant was the use of the Berg brick press as adapted to the pressing of wall tile.

In the afternoon the first plant visited was that of the Brush McCoy Pottery Company, where the processes involved in the casting and jiggering of pottery specialties proved interesting. At the J. B. Owens Tile Company, the structural beginnings of an Owen's tunnel kiln were observed and the details of construction and operation were explained. At the plant of the Ohio Pottery Company the manufacture of chemical porcelain was very interesting, this being one of the few plants in the country producing this line. The casting process is used for the most part in the forming of the ware and in burning, the European practice of a low temperature bisque and a high temperature glost fire is followed.

In the evening a banquet was held in the dining room of the Hotel Rogge. An informal program, including songs and speeches, was afforded.

Wednesday, June 26th:

In the morning the party visited the Roseville Pottery Company, Zanesville. A tunnel kiln used in the burning of art pottery and cooking ware was inspected. The party then proceeded to the plant of the American Encaustic Tiling Co. At this plant particular interest was evidenced in the clay storage bins and trolley systems, the use of compressed air in the slip presses, specially designed tile presses and the tunnel kilns employed in the firing of glazed ware.

In the afternoon an excursion down the Muskingum River on the Steamer Louise was enjoyed.

On Wednesday evening the party proceeded to the plant of the Kearns Gorsuch Company, where great interest was manifested in the processes of glass manufacture including the operation of automatic bottle blowing machines.

Thursday, June 27th:

In the morning the large paving brick plants of the Burton Townsend Co. were visited.

In the afternoon a motor trip was taken westward on the National Highway to the flint ridge district. Wilbur Stout, of the Ohio State Geological Survey, explained the ancient quarry workings where extensive operations were carried on originally by the moundbuilders and later by the American Indians. At one point the site of an ancient workshop in which primitive implements were made from the flint was visited. These flint implements have been found as far west as the Rockies, as far east as the Coast and from the Lakes to the Gulf. A number of specimens of these crude implements were found by members of the party. The moundbuilders' fortifications at the Golf Grounds, Newark, were next visited.

Proceeding to Buckeye Lake a shore dinner was served to the members at the resort hotel, after which a short business session was held.

Friday, June 28th:

The last day of the meeting was spent in visiting a variety of industries in adjacent towns, the first stop being the Ransbot-

tom Bros. Plant in Roseville, O. Modern jar machines and other equipment used in the manufacture of stoneware were explained and demonstrated. At the Crooksville China Company's plant at Crooksville, a rotary dryer, which had replaced the mold carrier and old style pottery dryer, proved interesting.

In the afternoon the plant of the A. E. Hull Pottery Co. was visited and the methods of manufacturing white tableware by the single fire process was demonstrated. A unique method of slip decoration was a feature. From this plant the party proceeded by train and trolley to New Lexington, Ohio, and visited the factory of the Ludowici Celadon Co. This factory is one of the most notable in the country and foremost in the manufacture of roofing tile. The operation of a shale planer, cutting a sixty foot face of shale, proved of unusual interest. The methods of raw clay storage and the preparation and feeding of the clay at this plant were exceptionally efficient. A producer gas fired continuous chamber kiln was explained. The methods of glazing and firing roofing tiles were also of special interest.

The last plant visited was that of the Ohio Brick and Stone Co. At the Company mine, flint fire clay is mined by the use of coal mining machines. The clay is then passed through a washing plant to remove the iron impurities which occur in soft seams in the flint clay strata. In the manufacture of fire brick at this plant a portion of the flint clay is ground in a wet pan and used as a bond in the forming of the brick by the dust pressed process.

F. K. PENCE, Chairman,
Committee on Summer Meeting.

THE HONOR* ROLL
OF THE
AMERICAN CERAMIC SOCIETY

Kenneth B. Ayer	F. Summer Hunt
H. H. Bartells	Charles E. Jacquart
Charles E. Bates	Joseph A. Martz
Harold A. Best	Fred A. Morgan
Clarence J. Brockbank	James S. McCann
John A. Chase	Edward Orton, Jr.
O. I. Chormann	Walter S. Primley
H. F. Crew	C. E. Ramsden
Kenneth I. Fulton	G. W. Rathjeins
Charles F. Geiger	H. S. Robertson
Albert C. Gerber	George M. Schaulin
Perry D. Helser	Charles W. Thomas
Herford Hope	E. H. Van Schoick
Walter L. Howat	William G. Whitford
Thomas N. Horsley	

* This list is not complete. Information in regard to those who are in some branch of the service and whose names are not included in the above list will be appreciated.

C. F. BINNS, *Secretary*, Alfred, N. Y.

JOURNAL OF THE AMERICAN CERAMIC SOCIETY

A monthly journal devoted to the arts and sciences related to the silicate industries.

Vol. 1

March, 1918

No. 3

EDITORIALS.

COÖPERATION.

The need of technical as well as economic coöperation in the Ceramic industry is unquestioned. In the new era upon which we are about to enter, coöperation will be the keynote of success.

More effective coöperation between our technical laboratories and our manufacturers appears to be one of the needs of the industry. This is especially true in the case of the small manufacturing industries which do not have the services of a technically trained staff at their disposal. Through the lack of technical guidance there has been a great amount of wasted time and effort in some instances. Laborious experiments and costly trials leading to no results have and are being constantly made. The lack of knowledge of some fundamental point has very often spelled the difference between success and failure. In the competition which is destined to come after the War it will be necessary to put our best into the industry. The methods of the past will no longer suffice.

In this connection it would appear that there has been a lack of coöperation and exchange of ideas among our technical laboratories. As evidenced by some of our literature of the past, there has been considerable duplication of researches and wasted effort. In several instances two laboratories have conducted parallel researches covering the same ground. This should not be, as our force of technically trained investigators is small and the field

of Ceramic research is large. Through the activities of the Committees on Ceramics of the National Research Council we have made an excellent beginning in the coördination of the war-essential researches. Why not coördinate the peace-essential researches through a central Research Committee as well?

HIGH TEMPERATURE FURNACES.

To our knowledge a satisfactory furnace for the determination of the softening or deformation points of fire clays and other refractories has not been placed upon the market. The gas furnaces do not reach the temperatures necessary to the softening of our most refractory products. The Deville furnace is unsatisfactory for several reasons. The granular carbon resistor furnaces have not come up to expectations. The vacuum furnace is expensive both as to first cost and maintenance. The method of determination of the softening points is being defined by our Committee on Standards. It is to be hoped that a satisfactory furnace for making the determinations will soon be found. *Inventors please take notice.*

INDUSTRIAL FURNACE SECTION.

The United States Fuel Administration has announced the complete organization of the Industrial Furnace Section, Bureau of Conservation, to handle fuel conservation in all furnaces with the exception of those operated for the production of power, heat and light. This includes those plants using fuel for direct heat, of which the clay products industries are the most important branch.

Mr. A. F. Greaves-Walker has been placed in charge of this Section and has under his immediate supervision 13 districts comprised of 31 states, covering the territory in which industrial furnaces are used. Each district has a local head who has in his organization an advisory board and a corps of inspecting engineers.

The newly appointed district chiefs met at the Fuel Administration Building, on July 29th, for a conference with the chief of the section. The district chiefs made reports based on a pre-

liminary survey of each district. Their conservative estimates of probable annual savings were 3,000,000 tons of coal.

The clay products, lime, cement and glass industries will be inspected first. A standard questionnaire is being furnished each plant owner in advance of the inspection, which he will fill out and hold for the inspector. The rating of each plant will be based upon the efficiency with which fuel is used. All wasteful burning processes will be taken into account, but an opportunity for correcting wasteful conditions will be given before inspection. Recommendations will accompany each questionnaire, several items of which will apply to each and every plant, and if followed will improve conditions materially. The inspecting engineer will be in a position to make further recommendations to each owner after inspecting his plant.

By appealing to the patriotism of the furnace owner, at the same time presenting tangible facts which show him a way of saving money for himself and fuel for the nation's use in the prosecution of the war, little trouble is expected in bringing about conservation of fuel through the proper regulation and operation of all industrial furnaces.

MEMBERSHIP CAMPAIGN

Although we are passing through the vacation period during which it is always difficult to secure action—the Committee on Membership reports the enrollment of an encouraging number of new members during the summer months.

An active campaign for members will be carried on during the fall and winter months and the organization of the industrial and professional divisions as provided for in the Rules will be continued. In this connection it is interesting to note that formal action has been taken by the New Jersey Clay Workers Association leading to their affiliation with the American Ceramic Society.

ORIGINAL PAPERS AND DISCUSSIONS.

SOME PHENOMENA IN GLAZE REDUCTION.

BY H. B. HENDERSON, Columbus, O.

In the development or finish of a number of wares, both decorative and utilitarian, reducing kiln atmospheres are important factors. We may refer to the employment of reducing fires in the production of hard porcelains, in the darkening of salt glazes, the change from dark brown to black, of red burning paving blocks and face bricks, and the golden flash on buff burning clay products.

The production of these effects has become a common practice and within reasonable limits, assuming the use of suitable materials, any desired effect may be produced by variations in the kiln atmosphere and of the duration of the treatment.

We were confronted with this question in making laboratory salt glaze tests on samples of clay. Clays were submitted with the request that we determine whether they were suitable for the production of salt glazed ware. Occasionally we secured favorable results and could report the material satisfactory, but attempts to duplicate the results on the same materials were negative from which it was evident that negative results on a laboratory sample did not safely justify an unfavorable report. The difficulty was explained, however, when we observed that satisfactory results were obtained and could be duplicated under exceedingly smoky kiln conditions accompanied by a deposition of carbon. It occurred to us that colloidal carbon deposited on and absorbed by the viscous surface of the piece might play an important role in the resultant color of the glaze. We know that a very light yellow salt glaze has been obtained in a contin-

uous kiln, under strongly oxidizing conditions, while wares from the same clay in a down draft kiln developed a dark brown glaze. At high temperatures, any kiln atmosphere, regardless of the gross oxygen content, has a somewhat reducing effect upon the wares being burned. If the dark brown color developed by the glaze in a down draft kiln is due to reducing conditions and the consequent presence of carbon, the light yellow color developed by the glaze in a continuous kiln, under normal operation, is also due to a reducing effect, the carbon possibly being the essential factor in both instances, though the quantity of carbon is not an important factor except in the development of color.

The above statement represents the theory upon which we have planned and carried out our investigations and the presentation of the subject at this time is merely a statement of progress without any attempt to draw final conclusions.

INVESTIGATION.

Sewer Pipe.—Samples of salt glazed sewer pipe were collected from different factories, and microscopic slides were made from fragments of the glazes. Under the microscope, even at low magnifications, the glazes were found to contain crystalline material and always of the same crystalline form, namely, hexagonal plates. One would not expect any crystalline carbon to be transparent and it does not seem reasonable that the crystals are graphitic although the carbon present may have influenced the crystallization of other constituents and affected the color.

Chippings of the glazes from pieces of the Akron and Junction City sewer pipe were found to contain 0.01 per cent. of carbon.

Samples of the clean glass drops taken from the roof of a kiln of the American Sewer Pipe Company, Uhrichsville, Ohio, were found to contain 0.014, 0.012, 0.016 and 0.017 per cent. of carbon, respectively. Under the microscope individual crystals, or several of them superimposed, could readily be studied by transmitted light.

In Fig. 1 is shown a microphotograph of a thin section made from a dark, mottled and very brilliant glaze occurring on a No. 2

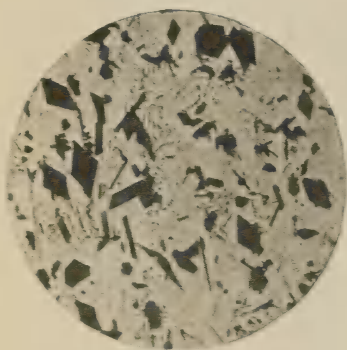


Fig 3

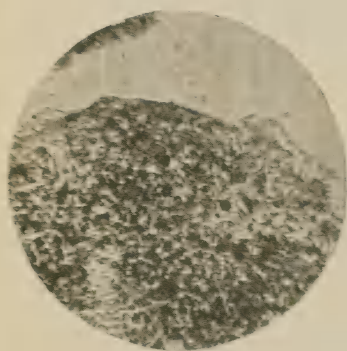


Fig 2

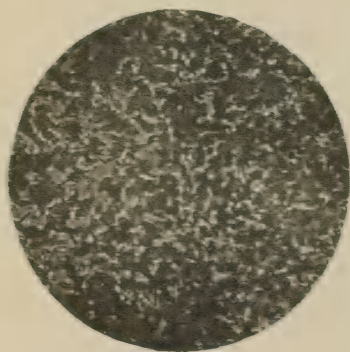


Fig 1

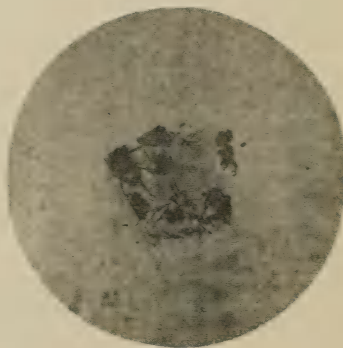
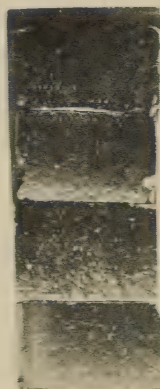


Fig 4



Fig 5



A B C D

Fig 6

fire clay body from Logan, Ohio—the dark spots being very small hexagonal plate-like crystals. In aggregates the crystals appear to vary from brown to black in color, but when separated, they appear amber colored by transmitted light. No particular form of grouping is noted.

In Fig. 2 is shown a microphotograph of a reddish colored glaze chipped from a sewer pipe made at Junction City, Ohio, from a mixture of shale and fire clay. Several slides were made from this glaze, using fragments of the normal glaze and also fragments from blotches of glaze which had dripped from the kiln crown. The latter fragments show an unusual growth of crystals and in one instance, where the drippings had collected on a socket of the pipe, the appearance was very similar to that of an iron oxide "aventurine" glaze. We made for comparison an "aventurine" glaze (Fig. 3), and in thin sections the crystals of this glaze appeared to be similar in form and color to those in the sewer pipe glaze, with the difference that the crystals in the former were larger, probably thicker and in consequence the color was more intense. In the "aventurine" glaze the crystals are undoubtedly ferric oxide.

In Fig. 4 is shown a microphotograph of a glaze chipped from a fire clay sewer pipe made at Uhrichsville, Ohio. The blackening of sewer pipe by a strong reducing kiln atmosphere is quite a common practice and excessive reduction has a tendency to produce crazing.¹ An examination of samples of sewer pipe, differing in shade in consequence of variations in the kiln atmosphere, shows an increasing number of crystals correlative to the darkening in color. In case of crazing, it is possible that the glaze, being heavily laden with crystals, is weakened probably by a difference in the coefficient of contraction between the crystals and the glaze matrix and, in consequence, fine hair-like cracks may develop when the proportion of crystalline matter becomes excessive.

In Fig. 5 is shown a microphotograph of a fragment taken from the surface of a fire flashed brick. The golden colors of flashed bricks are developed under the same conditions of kiln atmos-

¹ Karzen, *Trans. Am. Ceram. Soc.*, 18, 434 (1916).

phere as are those of salt glazed sewer pipe. If the crystals present in salt glazes were the result of the formation of sodium minerals, we would not expect to find them present in fire flashed products, in the development of which no salt is used. Samples representing various stages in the development of fire flashed bricks were prepared by scraping the surfaces with a hard steel tool, the dust thus obtained being mounted on slides.

Small particles of the crystallized material from the surfaces of the sewer pipe and flashed brick may be readily picked up and placed under the microscope by means of a needle point magnet. The magnetic properties of the crystals would indicate the presence of iron¹ in considerable quantity but not necessarily as a constituent of magnetite.

In order to illustrate the relative sizes of the crystals as shown in the microphotographs the following table of measurements is given. The measurements represent in each case the average of a large number of determinations.

Sample No. 1.....	0.00517 mm.	Sewer pipe, Logan, O.
" " 2.....	0.00517 "	Sewer pipe, Junction City, O.
" " 3.....	0.01696 "	Aventurine glaze.
" " 4.....	0.0168 ^o "	Sewer pipe, Dennison, Ohio.
" " 5.....	0.00266 "	Flashed brick.

Fig. 6 illustrates the variation in depth of color encountered on the same product differing only in the degree of burning. "A" is a thin weak glaze; "B" is a glaze of good golden color; "C" is dark brown; and "D" is dark brown and crazed.

A determination of the number of crystals per unit area relative to the number in "A" as unity gave the following results:

$${}^{\text{A}} = 1, {}^{\text{B}} = 6, {}^{\text{C}} = 25, {}^{\text{D}} = 20.$$

In D we find many imperfectly developed crystals, and perfect forms are seen entangled in a network of skeleton crystals. This condition is usually caused by very rapid crystallization.

Flashed Brick.—It has been generally maintained that the color of fire flashed ware is due to a chemical change

¹ *Trans. Am. Inst. Min. Engrs., Bull.* 126.

in the iron present in the product, but it is a well-known fact that the color can only be produced by exposing the surfaces of the ware to contact with the flame. The face of a brick so exposed will be beautifully flashed while the ends or back not so exposed, yet not in contact with other bricks, and consequently exposed only to the general reducing conditions of the kiln, will not be flashed. It is impractical to set the bricks in checkers because the flame in passing through the checkers will flash the surface under the open checker while the intermediate sections will not be flashed. The face of a brick so exposed is barred with alternate flashed and unflashed streaks corresponding to the checker work. It is evidently necessary that the flame impinge direct on the surface of the ware, but it does not follow that any dust is deposited on the surface. It might be that the local heating effect of the flame temperature develops a lower degree of viscosity, favorable to the growth of crystals, caused to develop in the reducing atmosphere, and thus furnishing nuclei for their continued growth during the subsequent period of oxidation in cooling. But we are of the opinion that the factor inducing crystallization is extraneous.

A flashed brick when reburned in a normal kiln atmosphere largely loses its flashed color and comes back to the natural buff color. It is a surmise whether the color of the crystalline material is eliminated during the oxidation or simply absorbed in the viscous matrix. We can conceive of the elimination of carbon but it would seem that the iron would tend to give a more intense color under the conditions of oxidation and solution following reduction.

Three samples of fire flashed bricks, all made from the same material and the product of one factory, were selected for examination. One had a pinkish color, which is not desired; one a good fire flashed color; and one a yellowish buff color, or simply a very light fire flashed effect. Under normal fire flashing conditions the pink color predominates but it is "burned out" by oxidation before closing the kiln. In addition to the above we had a series drawn from the kiln as the cooling progressed, showing the progression of the colors relative to the cooling.

All of these samples show the same hexagonal plate crystals found in the salt glaze. The tint of the pinkish colored sample is due to a few overgrown crystals of deep red color scattered among the mass of smaller ones of uniform size and light yellow color. The larger the crystals the redder the color, the very large ones approximating the color of the crystals in the "aventurine" glaze. The normal fire flashed sample contained a multitude of light yellow hexagonal plate crystals of fairly uniform size and color. The light fire flashed sample differs from the normal only in that there are fewer crystals. Trials drawn during the cooling process show a progressive increase in the number of crystals.

Refiring under reducing conditions retained or developed the fire flashed color, but a well flashed brick, refired under oxidizing conditions, largely lost its golden flashed color and developed instead a gray-buff color characteristic of a buff burning clay vitrified under oxidizing conditions.

An "old gold" flashed brick shows a mixture of crystals of different sizes and colors, the larger approaching the red and the smaller having the yellow color.

Reducing conditions are necessary to the introduction or development of the mineral constituents of the crystals, but the crystals are almost wholly developed under oxidizing cooling conditions, not that the oxidizing conditions are necessary—perhaps quite the contrary. We know that in flashed brick the high temperature oxidizing atmosphere not only destroys the crystals but eliminates a factor or so changes the mineral constituents from which the crystals form that we do not get a flashed surface. We also know, from practical experience, that a flashed effect on bricks can be developed at relatively low temperatures, but this effect lacks the true flashed color. Whether the color is due to iron or carbon the reducing conditions give a deposit on the surface of the ware—resulting in a dull lusterless flashed effect. At higher temperature there is surface fusion and in this fused mass the actual growth of the crystals takes place as the ware cools.

Briefly, in producing flashed brick we first subject the ware to reducing conditions, but if we continue this to the end, we sim-

ply blacken the surface. Instead, however, after reducing we burn out some of the black coloring element and start surface fusion. This is followed by additional reduction, partial burning out, the development of a greater degree of fusion, and thus alternating to the end. As an alternative, we carry on the oxidizing conditions until the surface fusion is accomplished, then reduce and finally eliminate any excessive reduction effect by oxidation, and finally cool slowly to develop the crystals.

If the color is due to iron, either in the clay itself or collected from the kiln gases, it is difficult to understand how this color can be burned out by subsequent oxidation except by the assumption of transformation and diffusion effects.

It is inconceivable that, in the cooling stage when the color develops, there can be any accumulation of iron from an outside source, but also inconceivable, were such accumulation possible, that it could be dissipated by subsequent reheating under oxidizing conditions. It seems probable that the intense color is an optical effect due to several modifications of crystals, or that the iron, in solution in the crystal, is in a molecular condition, giving a maximum color effect which largely disappears when the crystalline iron compound is transformed or decomposed. That several modifications of iron oxide compounds occur according to the prevailing oxygen pressure in the atmosphere seems to be an established fact. Again, it is possible that absorption by diffusion into the clay mass may occur.

The color system as applied by Sosman and Hostetter¹ indicates that the red and orange crystals contain an excess of ferric oxide while the yellow crystals have an increasing amount of ferrous oxide.

We must conclude, either, that the fire flashed color and the color of the salt glaze is not due to iron alone or, that the peculiar behavior in its development and disappearance above noted is due to physical changes. If the crystals are induced by carbon, their formation would be prevented under oxidizing kiln atmospheres and they would not develop in the subsequent cooling—unless the carbon be restored by an intermediate reducing kiln condition.

¹ *Trans. Am. Inst. Min. Engrs., Bull.* 126.

Summary.—Our preliminary work shows that both the salt glaze and the surfaces of fire flashed bricks contain crystalline matter; that these crystals have a red to yellow color to which the color of the product is due and represent ferric oxide or other modifications of iron oxide. It is likely that the color of the crystals is due both to a variable iron content, derived from the clay or the kiln gases, and modifications in the crystalline structure with variations in the temperature and oxygen pressure of the atmosphere; that the salt glaze contains carbon; that reducing conditions with the development of free carbon are essential for inducing crystallization; that crystallization hence starts in a reducing atmosphere but continues under oxidizing cooling conditions; that re-oxidation largely dissipates the color effect in flashed clay products.

DISCUSSION.

MR. PARMELEE: Is the firing under reducing conditions more favorable to the production of crystals?

MR. LOVEJOY: Mr. Henderson emphasizes the fact that the chippings from the glaze are magnetic, which indicates reducing conditions. He also quoted a statement made, I believe by Sosman, that the magnetic properties may be due to iron compounds other than ferrous oxide, to which the color may be due. Reducing conditions are necessary.

MR. PARMELEE: May not the presence of metallic iron account for the magnetic properties?

MR. LOVEJOY: No, it is an oxide.

MR. BINNS: Is it presumed that the color is due to colloidal carbon or to iron crystals? Both were mentioned.

MR. LOVEJOY: The author states that the color is due to iron and that the part the carbon plays is not understood. The presence of the carbon appears essential, however, not as regards the color, but as a factor in the development of the crystals. The crystals probably owe their color to the presence of iron. When flash brick are re-oxidized, the carbon present is probably elimina-

ted, and, in cooling, there is no development of crystals. If we reburn the brick under reducing conditions, we can restore the original flashed effect. The introduction of the carbon seems to be the essential feature in the development of the crystals—whether it is a chemical, physical, or mineralogical phenomenon, we do not know. In the absence of the carbon the crystals are not developed.

MR. PARMELEE: There is one point that is not at all clear. We have been shown that there is apparently a resemblance between the crystals developed in the "aventurine" glaze and those on sewer pipe; is it true that reducing conditions are necessary for the development of "aventurine" glazes? If "aventurine" glazes are not developed under reducing conditions, the relationship between the two is not quite apparent.

MR. MINTON: I have produced a number of "aventurine" glazes and have never resorted to reducing conditions. I have always considered that oxidizing conditions were preferable. Mr. Lovejoy emphasizes the importance of employing both reducing and oxidizing conditions.

MR. LOVEJOY: Mr. Henderson merely presented the "aventurine" glaze crystal to show its similarity to the salt glaze crystal. He does not state nor believe, so far as I know, that reducing conditions are necessary to the production of "aventurine" glaze crystals. In one salt glaze sample there was a glitter similar to that in an "aventurine" glaze which led to the comparison. He does not discuss the "aventurine" glaze nor claim any relationship between it and the salt glaze crystal other than crystal form and color. When we first began to use natural gas in the Hocking Valley, difficulty was experienced in securing the rich glaze color that had been secured with coal. The desired result was later accomplished without the use of coal by increasing the volume and pressure of the gas and curtailing the supply of air, in other words, filling the kiln full of unburned gases. My attention has recently been called to a practice which has been developed in connection with the burning of fire-flashed brick with coal. At the latter stage of the burn, a quart or more

of heavy oil is introduced into each furnace, the result being a very beautiful golden-flashed brick. The carbon undoubtedly plays some part in the development of these colors.

MR. WASHBURN: Attention has been called to the presence of carbon as a necessary condition in the development of the color. The effect of the carbon is to produce a certain definite concentration of carbon monoxide, and it is in this indirect manner that the reducing action takes place. The carbon itself does not appear to play any direct part in the action, but insures a definite concentration of carbon monoxide which apparently is the active reducing agent.

MR. BINNS: Some of those here can recall, in connection with the work of this Society, about 18 years ago, a discussion in reference to the development of flashed brick, and one of the members displayed a series of trials, drawn at periods from a kiln, showing that the trials when first drawn were blue, but the color gradually changed to yellow in cooling. Founded upon that fact, a theory was advanced which has been more or less the subject of discussion ever since—the formation of ferrous silicates. The thought which has been passing through my mind in that connection, applying to both this case and that of flashed brick, is that ferrous silicate has evidently formed and may be oxidized to the ferric silicate. If this is true, it accounts for the phenomena of flashed brick and also the yellow crystals in a carbonaceous magma. I think that this point explains the difference between the "aventurine" glaze and the crystal in the sewer pipe. In the "aventurine" glaze, the iron is added to the glaze and is readily available; in the sewer pipe the iron has to be dissolved from the clay and can only be dissolved when it is in the ferrous form. I have produced successful salt glazes in an experimental kiln without any reduction and have secured brown colors quite easily with no more reduction than is caused by a partial closing of the damper.

MR. STULL: Certain shades of amber glass are produced by dissolved carbon and the presence of a small per cent. of carbon in the glaze would account for the amber color. We know that

iron, under certain conditions, will also produce a yellow color. It is possible that the yellow color is enhanced by the presence of the dissolved carbon.

MR. BINNS: Why is it then, that in the burning of porcelain, the carbon stains the glaze black? The greatest difficulty in burning porcelain successfully, under reducing conditions, is the elimination of the carbon dissolved in the glaze. Why is it that the carbon stains the sewer pipe glaze yellow, and the porcelain glaze black?

MR. STALEY: In regard to the formation of ferric silicates, I would say that one encounters statements in ceramic literature to the effect that ferric silicates cannot be formed and that ferrous silicates are readily formed. We have, in mineralogical literature, repeated references to ferric silicates. In acid glazes one can introduce red ferric oxide, which, upon heating in the electric furnace, produces a yellow glass. There is no question in that case of the formation of a ferric silicate, without previous formation of ferrous silicate.

MR. BINNS: Mr. Staley has no proof that it is not a ferric solution.

NATURAL HYDRAULIC CEMENTS IN NEW YORK.

BY ROBERT W. JONES, Tompkinsville, N. Y.

It is impossible to determine the exact date when natural rock cements first came into use. In modern times the first structure, of any importance, in which this material was used was the Eddystone Light House, constructed by John Smeaton. The original discovery by Smeaton was in 1756. It was not until 1796, however, that the actual production of natural cements was made on a commercial scale. This material, produced from septaria, was patented by a Mr. Parker, under the name of "Roman" cement. Twenty-two years later the first production was made in the United States. The growth of the industry, in this country, has been closely associated with the construction of canals and other improvements of our inland water ways.

Limestones, after being burned, produce materials which can be conveniently classified under four heads, resulting chiefly from the varying amounts of impurities in the form of silica, iron and alumina. This classification includes common lime produced from the comparatively pure calcium or calcium-magnesium limestones; weak hydraulic limes carrying from ten to twelve per cent. of impurities; strong hydraulic limes with from eighteen to twenty-two per cent. of impurities, and hydraulic cement carrying as high as forty-two per cent. A large production of material reported from New York State as hydraulic cement should have been classified under hydraulic limes. The production of hydraulic limes, as a commercial industry of any magnitude, ceased many years ago. The following figures of production have been corrected, as far as possible, in regard to this production.

In 1768 was the first official notice of the desire for improvement of the inland navigation of the present State of New York. It was not until 1791, however, that any official act was passed looking towards the fulfillment of these desires. In that year there was appropriated by the State Legislature the sum of \$250 for an exploration and survey along the line of the present Barge

Canal. This work was completed under the direction of Benjamin Wright. In 1816 Mr. Wright was assigned as engineer in charge of the middle section of the Erie Canal with jurisdiction extending from the Seneca river to Rome, N. Y. Mr. Wright had as assistant engineer Mr. Canvass White. Mr. White, who was an engineer of great industry, made a voyage to Europe, at his own expense, to study canal construction. While in Europe the use of Taris and Roman cements, in hydraulic construction, was strongly brought to his attention. Mr. Benjamin Wright had recommended the importation of these cements for use on the Erie canal, but the great expense attached to this importation had worked against it and attempts were being made to complete the rock work with lime mortar. In most cases this was attended with complete failure.

In 1818 Mason Harris and Thomas Livingston entered into a contract to furnish lime for the middle section of the Erie canal. A quarry was opened on the property of T. Clark, Chittenango, Madison County. The burned material from this quarry lacked the usual characteristics of the ordinary lime in that it did not slake. Samples of this material being brought to the attention of Mr. White were recognized as being similar to the English Roman cements with which he was so familiar. After considerable experimentation patents were issued to Mr. White on February 1, 1820, and February 17, 1821, for the manufacture of natural cements for hydraulic purposes. There was considerable reluctance on the part of the Canal Commissioners and more on the part of the masons towards the use of this hydraulic cement. After a number of failures in the use of lime mortar, however, it came into universal use. In 1825 Mr. White brought suit against several contractors for non-payment of royalty, amounting to \$0.04 per bushel, and secured judgment. The contractors petitioned the legislature to relieve them of these judgments. The joint committee on Canals and Internal Improvements, believing in the justice of Mr. White's claim, recommended that he be paid the sum of \$10,000 to secure, to the people of the State, the free use of his cement. Mr. White accepted and a bill was introduced on February 11, 1825, read the first and second time, and committed to the committee of the whole

House. The bill died there and no further attempt was made to secure the payment.

In 1823 Mr. Wright was instructed to make a canal survey from tidewater, at the mouth of the Walkill, in Ulster County, to the Delaware river. This was to be known later as the Delaware and Hudson Canal. Construction began in 1825. Chittenango cement was used in the rock work during that year. Later in that year hydraulic cement rock was discovered near High Falls, Ulster County, but it was not until the summer of 1826 that the first commercial kiln was burned. This was at High Falls, and was operated by John Littlejohn. From this came the great industry which made Rosendale cement known, throughout the United States, as the standard natural hydraulic cement. After the completion of the rock work along this canal the local cement industry declined for a number of years and, until 1847, was carried on in a small way by a great number of producers. In that year came the first combination of operators and the production increased rapidly from an annual output of 200,000 barrels until in 1898 there was produced, from this section, almost 4,000,000 barrels.

For many years, after the discovery of the natural cement rock at Chittenango, there was great activity in the natural cement industry. Rock suitable for the production of this material was found at many localities along or in the neighborhood of the Erie canal and kilns were soon in operation throughout nearly the entire length of the canal. Soon after construction was begun on the Champlain canal, cement rock was discovered at Galesville, and quite a production was made for use on this canal. The construction of the Black River canal was responsible for the discovery and production of natural cement at Lowville, Martinsburgh, Depeauville and Waddington. This section supported quite an industry, although it declined rapidly with the close of canal construction. The more prominent localities along the Erie canal were Grand Island, Williamsville, Buffalo, Akron, Lockport, Oak Orchard Creek, Chittenango and the localities in and around Onondaga County. These were Fayetteville, Manlius, Edwards Falls, Jamesville, Marcellus Falls and Skaneateles Falls. Fayetteville began to produce in 1820 and

Williamsville in 1824. In 1839 Jonathan Delano erected works at Falkirk, near Akron, Erie County. In 1843 this business was passed on to James Montgomery and later transferred to Enos Newman. In 1854, H. Cummins and Son erected a plant at Akron. This was succeeded in 1865 by another plant. The Akron Cement Company was organized in 1870, taking over the plants of H. Cummins and Son. A few years later Cummins Brothers erected another plant west of Akron. The production



FIG. 1.—Behan's quarry, Manlius, Onondaga County, New York. The upper level of the quarry floor and the second heavy bed from the top of the quarry face were the productive cement layers.

of cement was carried on at Akron until 1909. This section was probably the greatest producer of hydraulic limes in the State.

The first cement made in Buffalo was produced by Warren Granger, in 1850. Lewis J. Bennett began the production of cement and organized the Buffalo Cement Company in 1874. This was an active producer of cement until 1902. The plants in Erie County are now all abandoned. The only other section, along the Erie canal, to become a permanent producer, was the Onondaga

County section. Production began at these localities almost immediately after the original discovery and has been continuous to the present time. The output of this section falls in a class between the true hydraulic cements and the hydraulic limes. It can hardly be classed as a true cement, although its characteristics place it closer to the cements than the limes.

The only other section making a continuous production was that of Howe's Cave, Schoharie County. The first kiln was

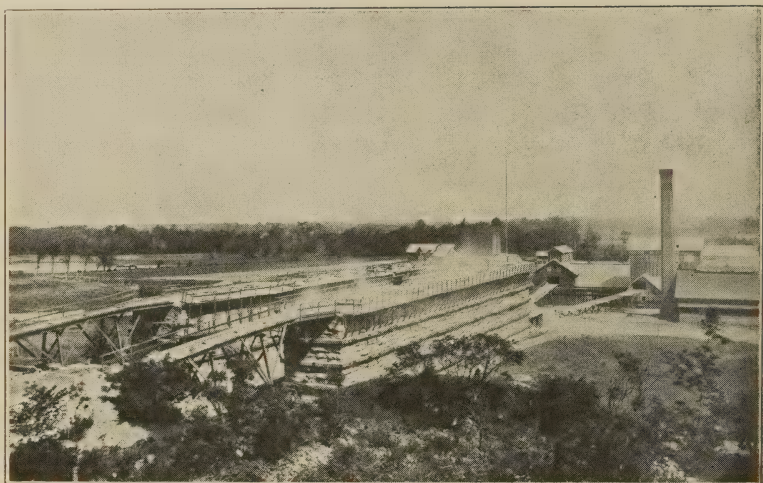


FIG. 2.—A continuous type of cement kiln, Cummings Cement Co., Akron, Erie County, New York. This was the type of kiln used by all of the Erie County producers.

burned at this locality by Mr. Vrooman in 1867. A few years later another plant was placed in operation and the two were productive until 1896, when they were consolidated and, after considerable reconstruction, production was again started in 1898, by the Helderberg Cement Company and carried on until 1905. At the present time, in the State of New York, there is one plant in operation in the Rosendale District and three in Onondaga County. The indications are that only one company

will celebrate the one hundredth anniversary of the discovery of natural cement in this State.

Geology.—The production of natural hydraulic cement has not been limited to any one formation, but includes limestones from the middle Ordovician to the upper Silurian. The lower, or oldest in the geological scale, is found in the Black River beds. The production from these beds was short lived and was consumed almost entirely in local construction. This material is included among the true cements, although of a rather poor grade. These



FIG. 3.—Opening in the cement layers at Akron, Erie County. A heavy layer of Onondaga limestone forms the roof.

beds have been productive to the extent of approximately 250,000 barrels. Next in ascending order comes the Rosendale water-lime, a subdivision of the Cayuga group of the Silurian. It is from these beds at High Falls that the original discovery, in the Rosendale region, was made and has been responsible for a production greater than any other section. Next in order come the Rondout water-limes of the Cayuga group. Rondout water-limes are exposed in the region between East Kingston and Kingston and have been extensively worked. The production from Buffalo,

Akron and Howe's Cave came from this horizon. The formation highest in the geological scale, which has furnished a commercial natural cement, is that of the Manlius limestone. Near the top of this formation, in Onondaga County, are found two thin beds from which the entire output of this section has been produced.

Mining.—In Onondaga County, due to the few feet of material available, the production of crude rock has been secured from open cuts and presents no features of unusual interest as regards min-

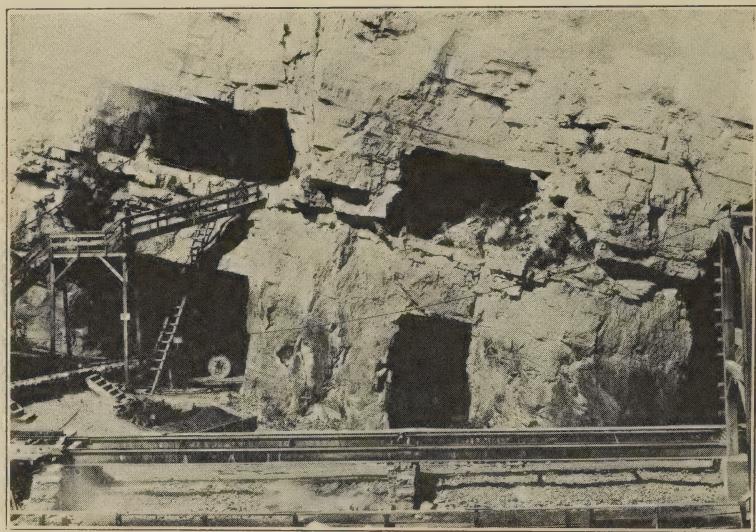


FIG. 4.—Openings of cement mines at Rosendale, showing method of mining along the productive beds.

ing. In the Buffalo-Akron district three of the four producers secured their crude material through underground mining. Adits were driven in along the outcrop, leaving heavy pillars of cement rock for support. The cement rock varied in thickness from five to eight feet. The roof, being of massive limestone, required only a very small amount of timbering. The Howe's Cave material was secured in the early days by open cuts and later by underground mining. It was in the Rosendale-Rondout

region that the greatest difficulties were encountered in the production of crude material. In this region the formations have been folded and faulted to such an extent that the entire output has had to be raised through inclines to the kilns. A distance of over eight hundred feet along the incline has been reached in one instance. The mine of the Consolidated Rosendale Cement Company, at Binnewater, is a typical example of mining in this region. At this property the main incline has an inclination varying from thirty-five to fifty-five degrees. There has been no attempt made to place the different working levels at any regular interval although the distance does approximate one hundred feet. On arriving at a point on the incline where it has been determined to drift along the beds, a cross-cut is driven across the three workable beds, which are known locally as the "old dark," "new dark" and "light." Between the "old dark" and the "new dark" beds is another bed of "light" which, on account of poor mining conditions, is not productive. Drifting is carried along the three beds in a northerly and southerly direction and at approximately right angles with the cross-cut. The slight grade of the drifts towards the cross-cut throws the drift line on a slight curve towards the east in order to keep out of the foot wall. At a distance of about sixty feet north and south from the cross-cut, along the "old dark" bed, inclines are driven downward along the bed. On reaching the determined new level, drifts are run connecting the two inclines and a raise is then driven along the bed in line with the main haulage incline. Rails are laid as the work progresses and, preferably at the end of a Saturday day shift, connection is made. On Monday the new level and incline is ready for use. At each level the opening of the haulage incline is equipped with a hinged door so arranged that when lowered the descending car passes over into the cross-cut and when raised allows the car to pass to the lower levels. There are six levels, the lower being used as a sump, the two upper not being productive on account of poor hanging walls. Very little timber is used and only at points where the hanging wall shows evidences of weakness. The working faces are carried with a width of about twenty-five feet and a height of eighteen feet. The entire output comes from the drift face and no attempt is

made towards stoping. Operations on the first and second levels had, in the early days, been let by contract with very poor results. The first level has been carried to the surface by frequent raises along the bed with very small pillars placed at irregular intervals and leaving very large rooms. It had been the intention of the present Company to mine the lower levels, leaving pillars of not less than forty feet in width.

Burning.—In the early days the raw material was broken roughly by hand and burned in crude upright kilns similar to those used in



FIG. 5.—Interior view of mine at Rosendale, Ulster County, New York.

burning lime. The walls were usually built of limestone and the kilns were sometimes lined with brick. Wood at first was the only fuel economically available. The fuel consumption was high and as soon as coal became more plentiful it was substituted for the wood. With the use of coal came the permanent upright kiln into which the crude rock and coal were fed in alternate layers and a certain amount of burned material removed every day. Rotary kilns were never used. The burned material was hand-picked, the underburned being fed back to the kilns or to a

special kiln and the burned being passed through jaw crushers and finally to millstones. After ageing, the material was shipped in paper sacks or wooden barrels.



FIG. 6.¹—Alvord and Company, Manlius, Onondaga County, New York. Old style of intermittent kiln now abandoned except in this district.

The following figures of production have been taken in most cases from original sources and may be accepted as the correct number of barrels of natural hydraulic cement manufactured in the State of New York since the discovery in Madison County. No attempt has been made to calculate the value per barrel. The production by districts is as follows:

Rosendale-Rondout district.....	85,873,000 Barrels
Erie County.....	14,300,000 “
Onondaga District.....	17,000,000 “
Howe's Cave.....	1,250,000 “
Miscellaneous.....	900,000 “
Total.....	119,323,000 “

¹ The preceding illustrations have been taken from cuts which have appeared in various reports of the New York State Museum.

TESTS OF CLAYS AND LIMES BY THE BUREAU OF STANDARDS PLASTICIMETER.¹

By F. A. KIRKPATRICK AND W. B. ORANGE, Pittsburgh, Pa.

¹ By permission of the Director, Bureau of Standards.

It is the purpose of this discussion to give the recent developments in the theory and use of the instrument described by W. E. Emley in the Transactions of this Society,² as the "Bureau of Standards Plasticimeter" as follows:

² *Trans. Am. Ceram. Soc.*, **19**, 523-33 (1917):

"When spreading a plaster on a wall, the trowel is so held that it makes an angle of 10° to 15° with the plane of the wall. The force applied to the trowel is thereby divided into two components, one acting parallel to the wall—the other acting normal to it.

"In the plasticimeter, the trowel is represented by a conical disk, which is mounted point downwards on a vertical shaft. The side of the cone makes an angle of 10° with the horizontal corresponding to the angle between the trowel and the wall.

"The wall is represented by a disk of plaster of Paris of known absorption. It is mounted on the upper end of a vertical shaft, directly below and concentric with the cone. This shaft is threaded and runs through a fixed nut. As the shaft revolves, the wall (or disk) is forced against the trowel (or cone) with a spiral motion. It presses vertically upwards against the cone in a manner analogous to that component of the force exerted by the trowel which acts normal to the wall. The turning motion moves the disk over the face of the cone bringing into play that component of the force which is parallel to the wall.

"The cone is so mounted that either of these forces is able to cause motion independently of the other. Any motion of the cone is transmitted through a system of levers to one of two bars, which are suspended like pendulums, and causes the bar to swing out of its originally vertical position. The greater the angle through which the bar is moved, the greater will be the force of gravity tending to return it and the cone to their original position. It follows, therefore, that if a constant force tends to cause motion of the cone, the bar will swing out until the force of gravity acting on the bar is in equilibrium with the force acting on the cone. When this condition has been attained, both the cone and the bar become stationary, and the force acting on the cone is directly proportional to the sine of the angle through which the bar has moved. The bars are graduated and provided with bobs which can be moved up or down thus decreasing or increasing the force required to produce a given angular deflection.

Calculating from the dimensions of the instrument as at present designed, we find the following relations:

$$v = 1.6 + 27.42 \sin a + 4.65 \sin^2 a.$$

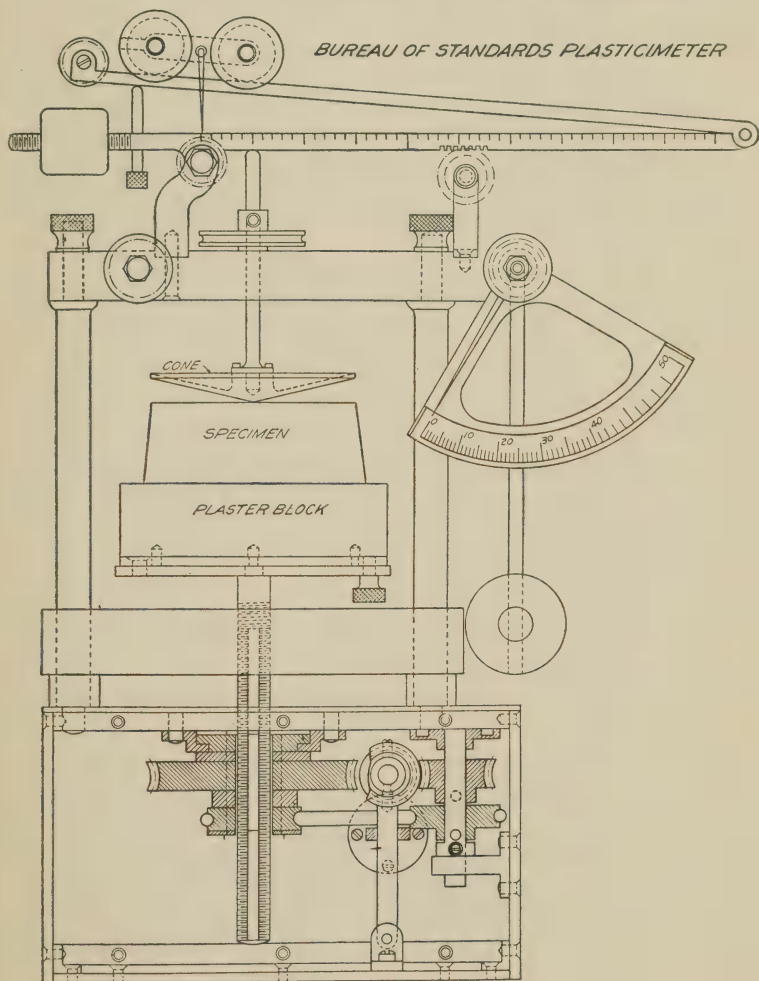
$$t = 9.29 \sin a + 1.577 \sin^2 a.$$

v = vertical force acting on cone, in grams per sq. cm.

t = tangential force acting on cone, in grams per sq. cm.

a = angle which the bar makes with the vertical.

l = distance from point of support of bar to top of bob, in cms.



"The independent term in the first equation is caused by the weight of the cone itself.

"If a sample of plaster is molded on the disk, and is driven against the cone at a constant speed, the two bars will assume definite positions. From these positions, the two forces acting on the sample may be calculated by means of the above formula. The vertical force corresponds to that component of the force actuating a trowel, which is normal to the wall, the tangential force corresponds to the component parallel to the wall. The machine is, therefore, capable of measuring independently the different forces which are applied to a trowel."

In the use of lime the word "plasticity" may be used to indicate the intrinsic plasticity of a paste which is not losing water to an absorbent surface; the rate of change of plasticity of a paste spread upon an absorbent surface; or the degree of workability of lime mortars. In each of these three cases different laws apply to the observed behavior of the materials. Hence, until more work has been done with the plasticimeter and the word "plasticity" is defined for the various materials, it is not advisable to offer the instrument as a universal means of measuring plasticity.

In the case of clays, it has not been determined whether or not the plasticity is actually measured by this instrument. The experiments with clays in the plasticimeter have been based upon the changes in plasticity when in contact with an absorbent surface. It was hoped that by the use of this instrument the relative values of clays and pottery bodies in the process of jiggering could be measured.

The authors of the present paper do not agree with Mr. Emley's calibration of the instrument so far as the tangential forces are concerned. In making this calibration he assumed that the forces acting in the horizontal plane, between the disk and the specimen, were of uniform magnitude in each unit area of the disk surface and hence that the total force could be considered as concentrated at a distance from the center equal to the radius of gyration of the surface of the disk. It is well known that the forces of friction vary with the speed. The speed of different portions of the specimen varies as the distance from the center and the forces of friction and adhesion are also subject to variation. The laws of these variations for lime pastes are not known

and considerable work will be required to determine them.

In view of these facts we have not used the equation given in Emley's article: In the present work the distance l was 12 cm. and was not varied. The sine of the angle a was used as "the relative tangential force." This method gave numbers which were proportional to the actual forces involved and eliminated the uncertainty of the calibration originally proposed. A measurement of the vertical forces has been found to serve no useful purpose.

Valuable results have not been obtained for either clays or limes by the use of a non-absorbent surface. In the tests herein reported a plaster of paris absorbent surface was used. As will be shown, contrary to Mr. Emley's contention, the results were found to depend upon the consistency of the clay body or the lime paste.

The method for determining the sand carrying capacity of the lime, as proposed by Mr. Emley, was found to be impracticable. Since the absolute value of the tangential force is not known, the work done upon the specimen cannot be calculated, although the general principle of the relation of work to the plasticity determinations in the plasticimeter still holds.

The method at present employed in the calculation of a plasticity or working quality figure for limes or clays is as follows:

The average relative tangential force for the period of time from zero to five minutes is called the "plasticity figure" of the clay or lime being tested. This method gives the most satisfactory values in a comparison of the plasticities of materials. If the limit of the machine is reached before the end of the five-minute period, the remaining values are obtained by extrapolation.

Method of Testing.

Limes.—Pastes were prepared from each hydrated lime. Each paste was covered with a damp cloth and, after standing at room temperature for from 16 to 18 hours, was molded into test pieces 3.15" in diameter and 1.5" high, the base being a plaster of paris block. The test pieces and plaster of paris block were then

placed in the instrument and revolved. As the water was absorbed by the plaster, the viscosity of the paste increased and the forces became greater—at a rate depending upon the rate of absorption. The relative tangential force was noted at intervals of 15 seconds—the instant at which the operator began to mold the specimen being taken as zero time.

In Fig. 1 are graphically shown the results secured on eleven hydrated lime pastes, the time being plotted against the relative

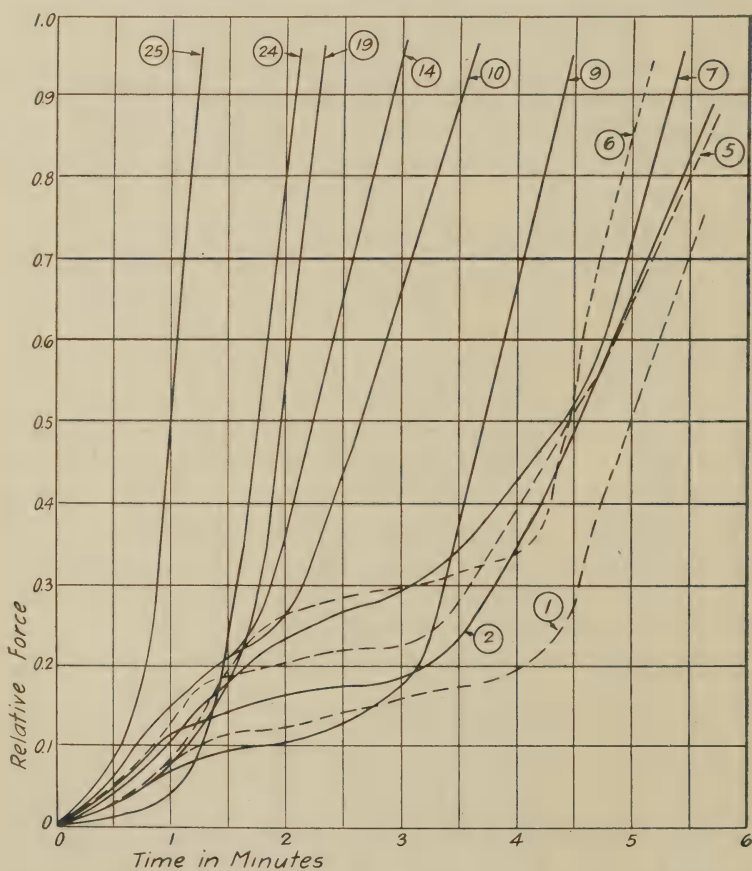


FIG. 1—Relation between time and relative force for hydrated limes in the Bureau of Standards Plastici meter

tangential forces. Since there is no accurate method of determining the degree of consistency of the pastes, three different consistencies were used and the one having the smallest value was chosen for comparative purposes.

Specimens Nos. 1 to 9, inclusive, are representative of plasters capable of being used commercially as finishing coats on walls. Up to a period of from 3 to 4 minutes the forces for these specimens are low after which they increase rapidly. Specimens Nos. 10 to 25 are not representative of commercial finishing coats. The forces for these latter specimens increase rapidly from the start, the form of the curves distinguishing them from those of the finishing limes. The average relative force for the period from zero to five minutes was calculated for each lime and the lower this average force, or "plasticity figure," the greater the plasticity of the lime. The results of the tests on the 25 hydrated limes are presented in Table 1. There seems to be no doubt that the plasticimeter has drawn a distinguishing line between the finishing and the non-finishing varieties of hydrated limes and has determined their relative behavior when spread upon absorbent surfaces.

Lime-Gypsum.—Owing to the fact that, in the preparation of finishing coats, burned gypsum is always added to hydrated lime, it was thought desirable to determine the working properties of lime-gypsum mixtures and the effect of the amount of water used in the preparation of the pastes. An Ohio finishing hydrated lime was mixed with amounts of water varying from 34 per cent. to 56 per cent., by weight. Each paste was allowed to stand from 16 to 18 hours and the "plasticity figure" was then determined in the plasticimeter. To a portion of each paste was then added 25 per cent. of burned gypsum (by weight of the dry hydrated lime), 0.25 per cent. of organic retarder (by weight of the dry burned gypsum), and sufficient water to give all of the pastes a like degree of consistency. This consistency was made to approach, as nearly as possible, that preferred by the plasterer in the coating of walls.

These mixtures were also tested in the plasticimeter. Some of the pastes were too soft to be molded and were placed in the machine in a container with the plaster of paris block at the

bottom. In this series of tests the test specimens were one inch thick instead of the $1\frac{1}{2}$ inches as ordinarily used. The results of these tests are given in Table 2 and shown graphically in Fig. 2. The percentage water in the lime-gypsum mixtures is not taken into account in the diagram, as these mixtures were all of practically the same consistency and water content.

TABLE 1.—“PLASTICITY FIGURES” OF HYDRATED LIMES.

No.	Source. (a)	Kind.	Plasticity figure.	Per cent. (b) water used.
1.....	Pennsylvania	¹ H M	0.163	42.5
2.....	Ohio	² H M F	0.227	43.6
3.....	Ohio	H M F	0.241	42.9
4.....	Ohio	H M F	0.244	43.6
5.....	Ohio	H M F	0.248	43.4
6.....	Ohio	H M F	0.277	44.4
7.....	Ohio	H M F	0.297	42.9
8.....	Vermont	³ H C	0.324	45.2
9.....	Ohio	H M F	0.332	42.9
10.....	Pennsylvania	H M	0.603	44.4
11.....	Maine	H C	0.620	44.9
12.....	West Virginia	H M	0.659	47.4
13.....	Pennsylvania	H C	0.663	50.0
14.....	Alabama	H C	0.751	46.4
15.....	Tennessee	H C	0.956	48.0
16.....	Missouri	H C	0.956	44.5
17.....	Pennsylvania	H C	1.01	41.2
18.....	Michigan	H M	1.23	42.9
19.....	Ohio	H M	1.25	46.0
20.....	Tennessee	H C	1.30	47.4
21.....	West Virginia	H C	1.35	47.4
22.....	Virginia	H C	1.37	50.0
23.....	Ohio	H M	1.43	43.6
24.....	Indiana	H C	1.93	48.0
25.....	Tennessee	H C	3.26	47.4

¹H M F—Ohio high magnesium finishing hydrated lime.

²H M —High magnesium hydrated lime.

³H C —High calcium hydrated lime.

(a) Samples received and tested in 1917.

(b) Per cent. of water to weight of the paste.

It will be noted that the curve for the lime pastes (Fig. 2) extends downward, from 38 per cent. water to the minimum plastic-

ity value at 48 per cent., and then rises. In other words, the 48 per cent. mixture is the most plastic of the lime pastes. The most plastic lime-gypsum paste however, is that made from a lime paste containing 38 per cent. water or 10 per cent. less than the amount required by the best lime paste. The question arises as to why the plasterer does not use 38 per cent. water instead of 48 per cent. in the preparation of his lime. His practice is probably governed by the fact that a 38 per cent. mixture would be so stiff and unworkable that the increased plasticity gained by using more water would not offset the increased amount of time required in the mixing.

TABLE 2.—EFFECT OF VARIATIONS IN THE WATER CONTENT OF THE PASTES ON THE PLASTICITY AND DENSITY.

Per cent. of water.	"Plasticity figures" of pastes.		Density of pastes.	
	Lime.	Lime-gypsum.	Lime.	Lime-gypsum.
34	...	0.560	1.56	1.52
36	0.705	0.271	1.64	1.53
38	0.780	0.210	1.57	1.53
40	0.709	0.252	1.53	1.49
42	0.567	0.355	1.52	1.49
44	0.527	0.304	1.50	1.49
46	0.454	0.525	1.47	1.51
48	0.447	0.485	1.45	1.48
50	0.486	0.520	1.42	1.48
52	0.527	0.538	1.40	1.48
54	0.675	0.590	1.38	1.46
56	0.695	0.695	1.35	1.45

The densities of the pastes are shown graphically in the lower part of Fig. 2 ("density," as here used, is the weight of a unit volume of the paste in grams per cc.). It will be noted that the densities of the lime pastes decrease uniformly from a value of 1.64 to 1.35 while the densities of the lime-gypsum pastes decrease from a value of 1.52 to 1.45. With an increase of water content the density decreases within the range of the amounts used—the highest plasticity not corresponding to the greatest density.

Clays.—The clays tested were ground to pass a 100-mesh sieve, sufficient water being added to produce the consistency necessary

for jiggering. The clay specimens tested were 3.15" in diameter and 0.25" thick. The reduced thickness of the specimen necessitated the use of a flat disk in place of the conical disk. After molding, and previous to testing in the plasticimeter,

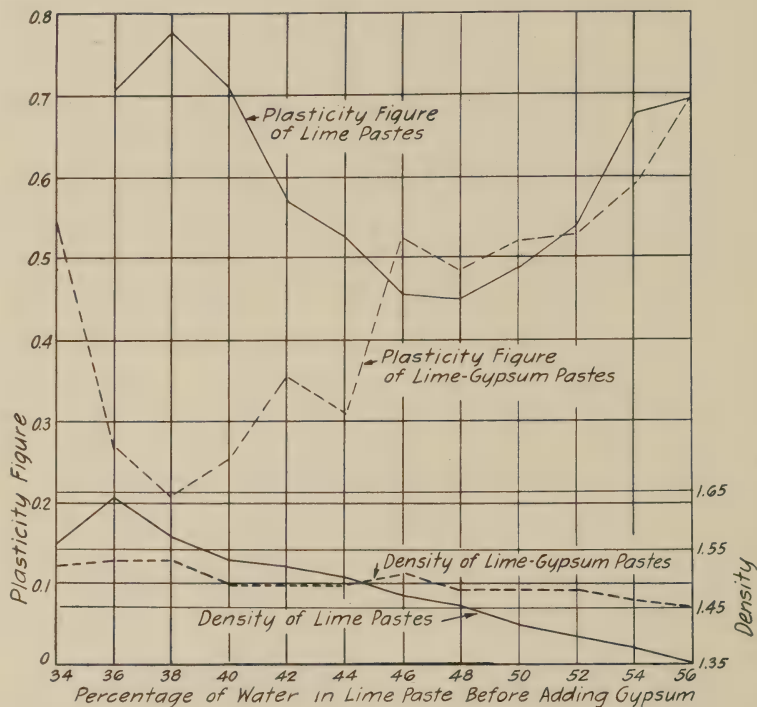


FIG. 2—Effect of consistency of lime paste on plasticity and density of the paste alone and with 25 per cent. gypsum.

the pieces were placed in a moist atmosphere for from 16 to 18 hours. The data secured for the clays is given in Table 3 and is shown graphically in Fig. 3.

It will be noted that the curves for the Tennessee and Kentucky ball clays, which we consider as being very plastic, are similar to those of the plastic limes while the curves of the non-

plastic kaolins are similar to those of the non-plastic limes. The relative behavior of the clays in jiggering appears to be indicated by the character of the curves. The action of the jiggering tool in pressing the clay against the plaster mold is quite similar to that of the plasticimeter disk in pressing the clay against the plaster of Paris block—hence the results should be comparable in either case. Sufficient investigative work has not been done to warrant the claim that the “plasticity figures” represent the relative plasticities of the clays, although they appear to give a comparative indication of the jiggering behaviors of the different clays.

TABLE 3.—“PLASTICITY FIGURES” OF CLAYS AND PORCELAIN BODIES.

Clay	F ₅ .	F ₃ .	F ₁₀ .
Tennessee ball clay.....	0.397
Kentucky ball clay.....	0.561
Illinois “kaolin”	0.567
Maryland kaolin.....	0.600
Florida kaolin.....	0.682
Georgia kaolin.....	0.790
New Jersey fire clay.....	0.879
North Carolina kaolin.....	0.992
English china clay.....	1.12
Delaware kaolin.....	1.37
Porcelain bodies:			
K1 (not aged)	1.05	...
K2 (not aged)	0.785	...
K3 (not aged)	0.645	...
K4 (not aged)	0.622	...
K5 (not aged)	0.483	...
No. 26 (not aged)	0.857
No. 26 (aged 8 months)	0.623
No. 34 (not aged)	0.937
No. 34 (stored 8 months)	0.650

F₅ = 0 to 5 minutes.

F₃ = 0 to 3 minutes.

F₁₀ = 0 to 10 minutes.

Porcelain Bodies.—A number of typical porcelain bodies were prepared in the usual manner and tested in the plasticimeter. Some of the bodies were tested at once while others were aged for

8 months previous to the testing. In the preparation of the bodies, sufficient water to afford the desired consistency for jigger-

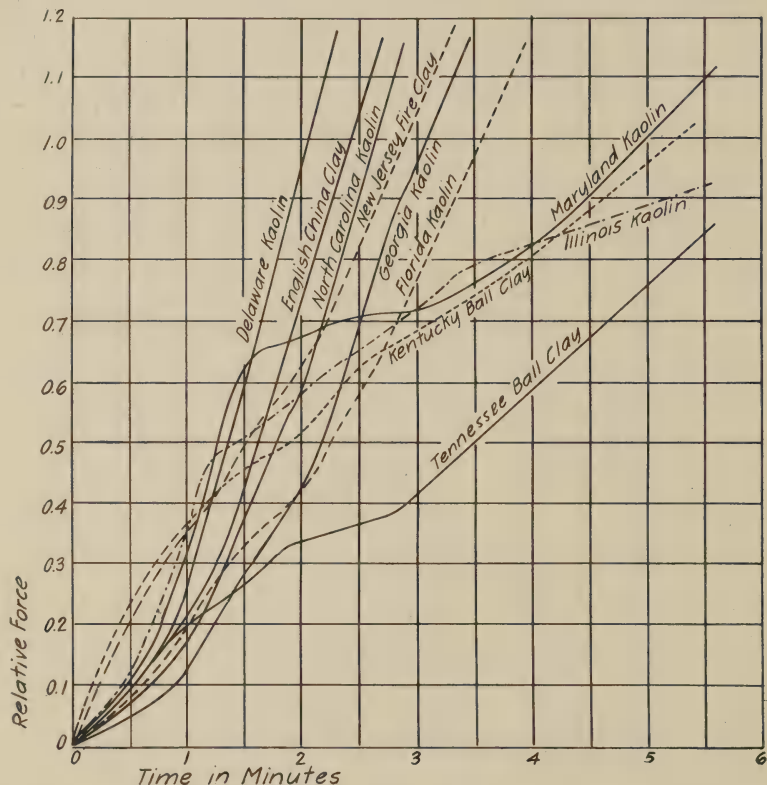


FIG. 3.—Relation between time and relative force for clays in the Bureau of Standards plasticimeter (using flat disk and quarter-inch specimens).

ing was added. The compositions of the bodies were as follows:

Body No. K1:	Per cent.
North Carolina kaolin.....	15.0
Georgia kaolin.....	15.0
Delaware kaolin.....	15.0
Feldspar.....	20.0
Flint.....	35.0
	<hr/>
	100.0

Body K₂—Same as K₁ with 4 per cent. Tenn. and Ky. ball clays replacing 4 per cent. of the kaolin.

Body K₃—Same as K₁ with 8 per cent. Tenn. and Ky. ball clays replacing 8 per cent. of the kaolin.

Body K₄—Same as K₁ with 12 per cent. Tenn. and Ky. ball clays replacing 12 per cent. of the kaolin.

Body K₅—Same as K₁ with 16 per cent. Tenn. and Ky. ball clays replacing 16 per cent. of the kaolin.

BODY NO. 26.		Per cent.
N. Carolina kaolin.....		12.5
Florida kaolin.....		12.5
Delaware kaolin.....		12.5
Georgia kaolin.....		12.5
Feldspar.....		20.0
Flint.....		30.0
		100.0

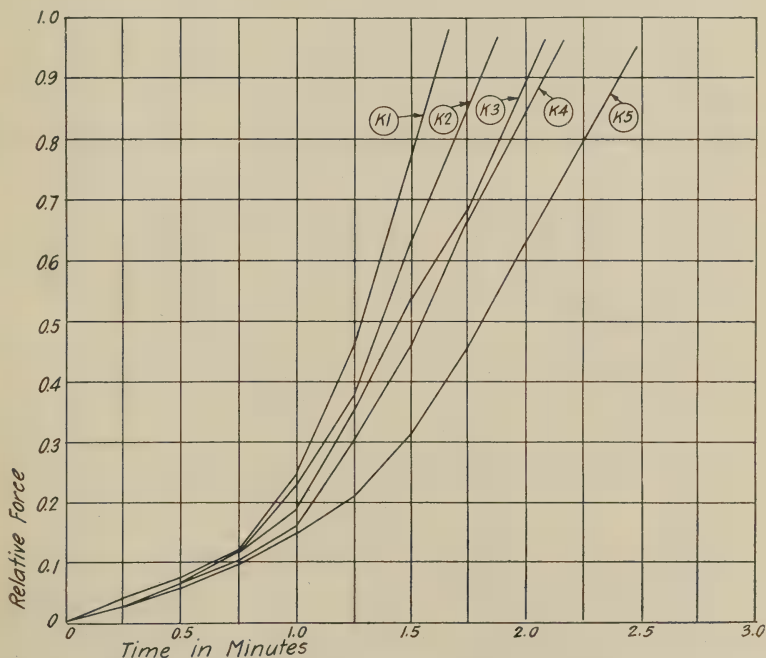


FIG. 4.—Relation between time and relative force for porcelain bodies in the Bureau of Standards plasticimeter (using flat disk and quarter-inch specimens).

BODY NO. 34.		Per cent.
N. Carolina kaolin.....		13.75
Florida kaolin.....		13.75
Delaware kaolin.....		13.75
Georgia kaolin.....		13.75
Feldspar.....		18.5
Whiting.....		1.5
Flint.....		25.0
		100.00

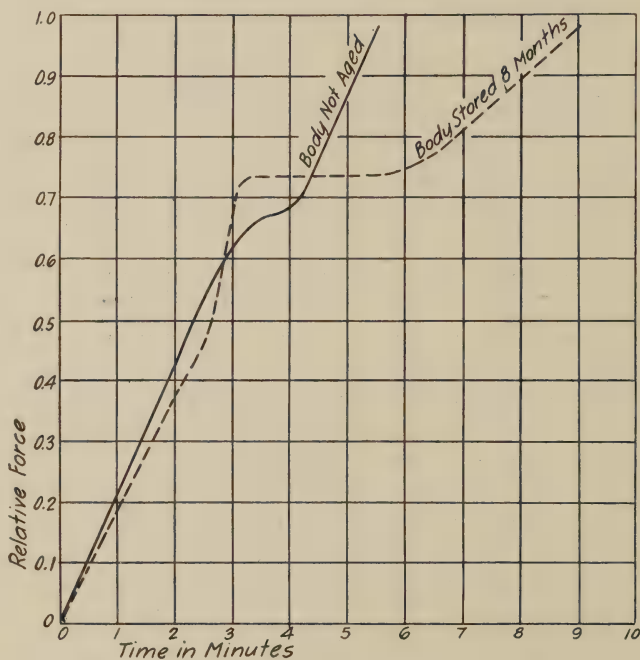


FIG. 5.—Relation between time and relative force for porcelain bodies in the Bureau of Standards plasticimeter (using flat disk and quarter-inch specimens).

The results of the tests upon the porcelain bodies are given in Table 3 and are shown graphically in Figs. 4 and 5. Test pieces $\frac{1}{4}$ " thick were prepared from bodies K₁ to K₅, and the "plasticity figure" represents the average relative force for the period

from 0 to 3 minutes. An increase of the ball clay content apparently causes a uniform decrease in the "plasticity figure" with the exception of those for bodies K₃ and K₄ which are quite close together.

Specimens $\frac{1}{2}$ " in thickness were prepared from bodies 26 and 34 and the "plasticity figure" calculated for a period of time from 0 to 10 minutes. The results are given in Table 3 and shown graphically in Fig. 5. The ageing of the bodies for 8 months has materially improved their jiggering qualities.

Conclusion.

It should be noted that the determinations on the clays are not numerically comparable with those for the limes since different weights were used on the pendulums in the testing of the two materials.

It may be said that the plasticimeter has given us some practical information in reference to the properties of hydrated limes and of clay bodies. There is room for improvement, however, in the mechanical construction before the instrument may be employed in correlating plasticity with the other properties of the materials.

It remains to be proven whether the property of retaining water and the resistance to deformation under pressure is a measure of the plasticity of a ceramic body when in the plastic condition.

COMMUNICATED DISCUSSION.

W. E. EMLEY: I want to thank the authors for the above criticism. If the instrument had not been criticized it would in all probability have died a natural death as so many plasticimeters have done before. It has now received a new lease on life, and I hope that further experiments will bring to light the defects in the present design and help to perfect it.

It is unfortunate that the authors have found it necessary to establish certain empirical conditions for the use of the instrument—such as the consistency of the paste, the thickness of the specimen, the duration of the experiment, etc. This makes it difficult, or rather impossible, to compare the results obtained

under different conditions. The fact that the "plasticity figure" has no absolute meaning blocks any attempt to correlate the plasticity, as measured, with any of the other physical properties of the materials. This subject is worthy of thorough and careful investigation. Even though it should be found impossible to design a machine which would measure plasticity in c. g. s. units, the attempt to do so would undoubtedly contribute largely to our present meagre knowledge of this subject.

It is very gratifying to note the definite statement that the instrument is able to differentiate between finishing limes and other limes. This is the purpose for which the instrument was designed. At present the only way of making such a distinction is by actual trial—by having the lime spread on a wall by a plasterer. This method is not satisfactory. It is too laborious and the results depend upon the personal opinion of the laborer—who is frequently not any too intelligent and is apt to be biased. Such results cannot be expressed in black and white for future reference. It is therefore of great benefit to the industry to have an instrument which can measure and express different degrees of plasticity—even though the results are only comparative, and not absolute.

It is very interesting to know that the instrument gives an indication of the behavior of clays in jiggering. The plasticimeter was not designed for this purpose. This would indicate that the instrument may be adaptable to a wider field of usefulness than has as yet been contemplated.

I glean from the present paper that the instrument is, as now designed, capable of practical use in studying the plasticities of limes. This should facilitate and stimulate the redesign of the instrument to overcome the present technical faults. I hope that the authors will continue their experiments along these lines.

THE USE OF FURNACE SLAG AS GROG IN ARCHITECTURAL TERRA COTTA BODIES.

BY R. H. MINTON, Metuchen, N. J.

One of the most interesting and important ceramic products, architectural terra cotta, has within recent years fallen into some disrepute on account of a few cases of failure in the building, one common type of failure being so-called "dunting." This is unfortunate because terra cotta lends itself to the modern system of steel construction better than any other type of building material.

Very little has been published on this subject. R. L. Clare¹ states that "the first and most important cause of failure is a defective body mixture." He also states that "experiments which we have made indicate that it is much easier to produce fire cracks or cooling cracks by a slight change in the rate of firing and cooling than it is by changing the body composition over a wide range."

In an investigation of the "dunting" of architectural terra cotta, E. C. Hill² states that, "fire cracking seems to depend almost entirely on two factors, namely, the composition of the body and the rate and method of cooling. Regarding the composition, it was noted that bodies composed of very sandy clays are much more sensitive to fire cracking than those made of less sandy, more plastic clays." His final conclusion was that "while cooling is of the greatest importance, the composition and density of the body are large factors in the sensitiveness of the body to fire cracking."

Hill is undoubtedly correct in his belief that the body should be controlled by the size and the amount of the grog, rather than by the use of sandy clays, but he seems to have overlooked

¹ *Trans. Am. Ceram. Soc.*, 19, 593.

² Not published.

the question of the *kind* of grog. The kind of grog is undoubtedly of equal importance to the size and the amount.

Some years ago our attention was drawn to the possibility of using furnace slag as grog in terra cotta bodies, the slag being a material of low cost, light in weight, and possessing sufficient resistance to destruction by the elements. Preliminary tests which we conducted with this material were not satisfactory, on account of the inferior quality of the slag selected, but recently our experiments with slag for this purpose have been quite promising.

In our first experiments we used ordinary crushed slag but it was found that granulated slag, on account of its lightness in weight and freedom from iron, etc., offered greater possibilities. It was soon determined that we were limited to the use of acid slags, the basic slags being unsatisfactory as grog on account of their excessive weight and their content of free lime which would probably cause disintegration of the burned terra cotta bodies. The following two bodies are typical of those prepared in our investigation:

Body No. 174.

Stoneware clay	15 parts (by vol.)
Retort clay	15 parts (by vol.)
Slag	20 parts (by vol.)
BaCO ₃	1/2 per cent.

Body No. 175.

Stoneware clay	15 parts (by vol.)
Retort clay	15 parts (by vol.)
Grog (sagger)	20 parts (by vol.)
BaCO ₃	1/2 per cent.

A granulated slag from Coatesville, Pa. having the following composition was used in Body No. 174:

	Per cent.
SiO ₂	44.1
Al ₂ O ₃	24.1
Fe ₂ O ₃	1.3
CaO.....	20.6
MgO.....	6.7
MnO.....	3.0
	<hr/>
	99.8

The test pieces were burned in a coal-fired test kiln with cone 5 turning at the end of a firing period of 45 hours. At cone 5, Body No. 174 develops a dark buff color and Body No. 175 a light buff color. Both bodies develop a good dense structure when fired to this cone.

Freezing Tests.

After boiling for three hours in a sodium sulphate solution, the test pieces were removed and dried at room temperature for 48 hours—the immersion and boiling treatments being repeated a number of times. No apparent effect of this treatment was observed on either body up to the fifteenth test, after which Body No. 175 began to flake slightly. Body No. 174 was not affected after being subjected 34 times to the treatment. The condition of the two bodies at various stages of the treatment was noted as follows:

flakes.....B 174 not affected.

The condition, after the 34th treatment, of two of the shrinkage bars was as shown in Fig. 1. It will be noted that Body No. 174 was practically unaffected by the sodium sulphate test while Body No. 175 is partly disintegrated and has the appearance of a rock-faced building brick.

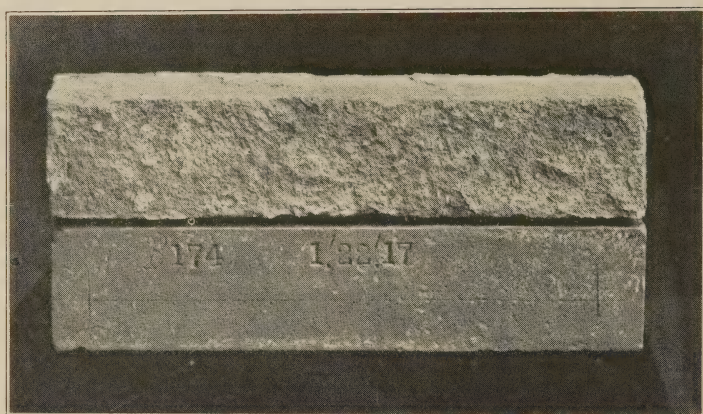


FIG. 1.—Bodies Nos. 174 and 175 after 34 sodium sulphate treatments.

In order to determine the resistance of the two bodies to actual freezing, pieces of each were immersed in water until saturated, thoroughly frozen at 5° F., and then thawed. Both bodies were apparently unaffected after having been frozen and thawed twenty-five times. The compressive strength of the two bodies, before and after the natural freezing, was as follows:

	Compressive strength, pounds per sq. in. (Before freezing.)	Compressive strength, pounds per sq. in. (After freezing.)
Body No. 174.....	6710	6410
Body No. 175.....	5900	3660

It will be noted that the freezing treatments have affected but slightly the compressive strength of Body No. 174, whereas the compressive strength of Body No. 175 was reduced about 40 per cent.

Experimental Bodies.

In order to compare the slag type of body with others, a number of mixtures, in which were used sagger grog, slag, slag and sagger

grog mixtures, and vitrified porcelain grog as the non-plastic ingredients, were prepared as follows:

Body No. 200—commercial terra cotta body	
“ No. 201—commercial terra cotta “	
“ No. 202—commercial terra cotta “	
“ No. 203—Stoneware clay	15 parts (by vol.)
Retort clay	15 parts (by vol.)
Grog (sagger)	20 parts (by vol.)
BaCO ₃	1/2 per cent. by weight
“ No. 204—Stoneware clay	15 parts (by vol.)
Retort clay	15 parts (by vol.)
Grog (sagger)	10 parts (by vol.)
Granulated slag	10 parts (by vol.)
BaCO ₃	1/2 per cent. by weight
“ No. 205—Same as Body No. 204 but containing	
20 parts of slag	
“ No. 206—Same as No. 204, but containing 20	
parts of electrical porcelain grog	
“ No. 207—Stoneware clay	15 parts (by vol.)
Retort clay	15 parts (by vol.)
Grog (sagger)	16 parts (by vol.)
Granulated slag	4 parts by (vol.)
BaCO ₃	1/2 per cent. by weight

The granulated slag used in Bodies Nos. 204 and 205 had the following composition:

	Per cent.
SiO ₂	32.4
Al ₂ O ₃	12.2
CaO.....	39.3
MgO.....	11.6
MnO.....	0.8
S.....	1.8
	<hr/>
	98.1

The slag used in Body No. 207 was from the Illinois Steel Co., the composition being as follows:

	Per cent.
SiO ₂	34.2
Al ₂ O ₃	12.4
CaO.....	47.5
MgO.....	3.6
Fe ₂ O ₃ MnO.....	0.9
S.....	1.7
	<hr/>
	100.3

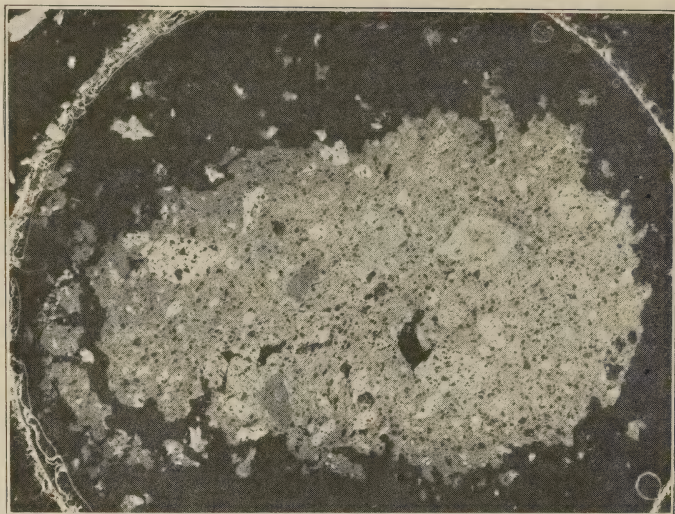


FIG. 2.—No. 202, Commercial terra cotta body.

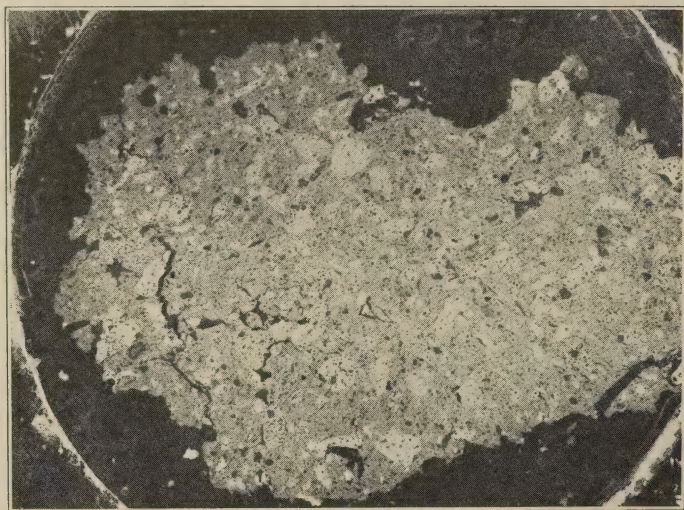


FIG. 3.—No. 203, Experimental body, similar in composition to commercial body.

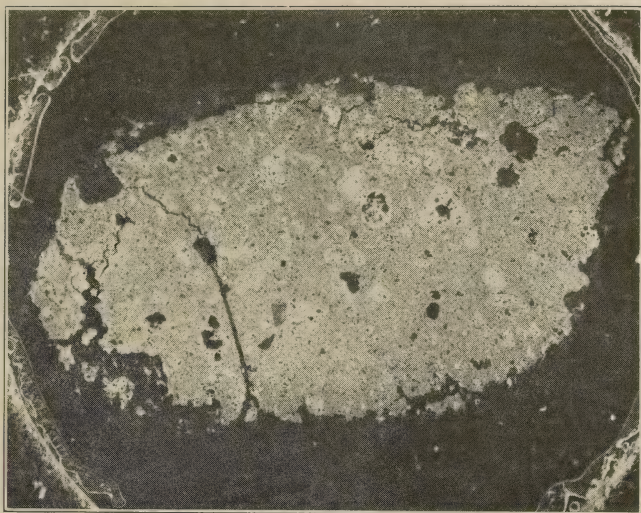


FIG. 4.—Body No. 205, containing 20 per cent. slag as grog.

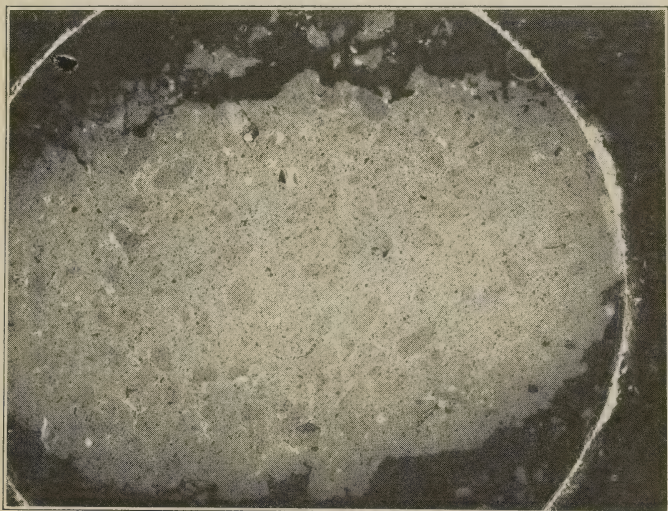


FIG. 5.—Body No. 206, containing 20 per cent. crushed porcelain as grog.

In Figs. 2, 3, 4 and 5 is shown the structure afforded by the different types of grog in Bodies Nos. 202, 203, 205 and 206, respectively. The photographs were taken of a section of each of the bodies after grinding to a smooth surface on a carborundum grinder.

The shrinkage, absorption, and crushing strength of each body was found to be as follows:

Body No.	Per cent. burning. Shrinkage. (Basis dry length.)	Per cent. absorption. Burned to Cone 4-5.	Crushing strength. Burned to Cone 4-5.
200	3.5	10.9
201	2.9	11.1	4600 lbs. per sq. in.
202	4.9	11.9
203	3.9	11.0	3250 lbs. per sq. in.
204	4.9	7.2	4325 lbs. per sq. in.
205	5.0	10.1	3490 lbs. per sq. in.
206	5.9	7.6	5300 lbs. per sq. in.
207	3.5	13.4	3325 lbs. per sq. in.

The results of the sodium sulphate tests made on these bodies may be summarized as follows:

After 50 treatments.

- No. 200—Scaling considerably at one end.
- 201—Scaling somewhat.
- 202—Scaling slightly at one end.
- 203—Flaking considerably on edges.
- 204—Very slightly affected on bottom surface and edges.
- 205—Only slightly affected.
- 206—Flaking on the edges.
- 207—Flaking considerably at one end.

The treatments will be continued until complete disintegration has taken place. After fifty treatments bodies Nos. 205 and 206 were the least affected. It was to be expected that a body containing electrical porcelain, stoneware, or a similar vitrified grog would be more resistant than one containing fire-clay grog. However, the vitrified grog is not obtainable in large quantities is heavier, and detracts from the working properties of a body.

Conclusion.

If further experiments confirm the practicability of the use of slag as grog in architectural terra cotta, an abundant material

at less than one-half the cost of sagger grog, and also considerably lighter in weight, is available. In the selection of a slag, careful attention must be given to the source and quality—we have found the granulated slag to be the best for this purpose. In the above experiments we have experienced little difficulty from the presence of iron in the slag but this is a matter which would require some attention. Any iron present may possibly be removed by passing the slag over a magnetic pulley.

This opportunity is taken to express our appreciation for the assistance of Mr. E. Ogden in making the freezing and crushing strength tests.

COMMUNICATED DISCUSSIONS.

P. H. SWALM: To the many theories for the causes of "dunting" Mr. Minton's investigation adds one to be well considered. Is the nature of the grog a factor in "dunting?" Unfortunately, for lack of better tests, his conclusions are based upon the disintegration or flaking of the body and his crushing strength data. Is it not a fact that the stronger bodies which resist disintegration are also subject to the fault of sudden rupture or "dunting?" This has been my experience with fire clay sanitary ware bodies.

It is possible to understand why a body gives way under rapid cooling in the kiln, and it is to be expected that a dense body, improperly bonded, might "dunt" under strain at some later time, but it seems to me that the "dunting" of a well bonded strong body at a delayed period may only be caused, either by a defect in molding or by the unusual physical properties of one of the ingredients of the body. By the use of tight burning, sandy, heavy fire clays, I have produced fire clay sanitary bodies of apparently good quality, but found that these bodies "dunt" very readily, regardless of the size, quantity, and vitrification behavior of the grog used. This was probably due to the introduction of an excessive amount of silica as like results were secured by the substitution of coarse sand for the fire clay grog.

The properties of the grog must therefore be considered. Mr. Minton's investigation shows that by the use of slag a stronger and more resistant body is produced but the effect on "dunting"

is not conclusively proven. I have found that the use of electrical porcelain grog improved the body, but I could not entirely eliminate the sagger grog from the mixture on account of the reduction in strength in the raw clay state. The porcelain grog, being vitrified, is not conducive to a firm bond between the grog and the clay. The latter point is one to be well considered in the use of the slag as grog in fire clay bodies.

H. W. MOORE: The terra cotta companies have, for at least two years back, been trying to improve the quality of their bodies and the use of slag as suggested by Mr. Minton is, so far as I know, something entirely new. I have tried a sample of slag myself, but found it unsuitable for this purpose. If, by the use of the slag from the Midvale Steel Company, it is possible to produce a body which will successfully resist the sodium sulphate tests as applied by Mr. Minton, obviously, a great stride in the improvement of terra cotta bodies has been accomplished, as, in my opinion, such a body would withstand any atmospheric exposure to which it would be subjected.

E. C. HILL: Mr. Minton, in advocating the use of furnace slag as grog in architectural terra cotta, has introduced a material that is new to the industry, but which may prove of considerable importance in the future. If slag is available at one-half the cost of broken saggars, as Mr. Minton states, and can be obtained free from impurities and constant in composition, its use is certainly worth considering.

Mr. Minton refers to failures of terra cotta due to "dunting" and suggests as a remedy the use of slag as a source of grog instead of saggars. The results show that the slag body has a much lower absorption and greater crushing strength than the sagger body and successfully withstands the artificial freezing test with the sodium sulphate solution while the sagger body fails in this test. His conclusions, based on this test, are that the slag and vitrified porcelain bodies are more able to withstand the action of the weather than the sagger body, although he attributes the failure of terra cotta in practice to be chiefly due to "dunting."

The failure of terra cotta from "dunting" is due to its inability to withstand changes of temperature, involving the expansion and contraction of the piece, and not to its inability to withstand disintegration or flaking off, due to the destructive action of freezing and thawing. When terra cotta fails from "dunting" the piece is broken or cracked in sharp lines, the fracture being smooth and cleancut; when it fails from disintegration, due to freezing and thawing, the failure is evidenced by crumbling of the edges and the flaking off of the sides.

The character of the failure produced by the artificial freezing test, crumbling and flaking of the piece, would be expected from the continued action of natural freezing and thawing but I have never observed the sharp hair-line cracks, so characteristic of "dunting," in any of the test pieces subjected to the sulphate treatment. I do not think that "dunting" cracks could be produced by this treatment unless the pieces were quite large, in which case a failure would be more likely to result from the continued rapid heating and cooling than from the disruptive action of the crystallized salt from the sulphate treatment.

Bureau of Standards Report.

In this connection, I would quote the following from a report of the Bureau of Standards, dated May 10, 1918, to the National Terra Cotta Society, concerning an investigation of terra cotta bodies: "The value of this test (artificial freezing) as a criterion of the weather-resisting properties of a body is open to some question. The appearance of the disintegrated specimens closely resembles that shown by terra cotta which has failed in service, due to alternate freezing and thawing, although similarly prepared specimens have been frozen and thawed 37 times during the past winter and do not show at all the same behavior. Only 8 cubes (4" solid) show any effect of the natural freezing and it consists of a clean, sharp break of the cube into two fragments. None of the open boxes (8" \times 8" \times 6" deep with 1" walls) show effects of any kind caused by the same number of freezings. According to Staley,¹ one sodium sulphate treatment of clay drain tile is equivalent to two natural freezings, if the tile in the

¹ *Trans. Am. Ceram. Soc.*, 18, 642-923 (1916).

latter case are partly immersed in the water while freezing. In the present investigation no such ratio has been obtained for some of the specimens disintegrated at the end of two sodium sulphate treatments but were intact at the end of 37 natural freezings, a ratio of 1 to 18. The terra cotta specimens were, however, not immersed during the freezing but were saturated with cold water."

Theory of "Dunting."

(E. C. HILL.)

Terra cotta bodies giving the best results in the artificial freezing tests are those that are hard and dense and having comparatively low absorption and high compressive strength. A body of this kind would, in all probability, be more sensitive to "dunting" than one less dense and would have a correspondingly higher absorption and lower strength. In a paper read by the writer before the New Jersey Clay Workers' Association, June, 1917, on fire cracking or "dunting" in terra cotta, from which Mr. Minton has quoted, the causes of "dunting" were discussed as follows: "The failure due to "dunting" is evidenced by sharp hair-line cracks in the piece either occurring in the kiln or appearing later when set in the building. The cracks are more liable to occur on large pieces of heavy cross-section than on the smaller, lighter pieces. When the cracks appear in the building they are more likely to be found on pieces which are exposed on all sides than on those set in the wall. The cause of the failure by "dunting" is attributed to strains set up in the body during cooling. These strains produce the hairline cracks at the time, or cause cracking later when the pieces are subjected to changes in temperature. Experiments made show that fire-cracks may be produced in all bodies by rapid cooling and that, if cooled slowly enough, all bodies are free from the fire-cracks.

Regarding the composition of the body, it appears that the hard, dense bodies are more sensitive to fire-cracks as are also those containing very sandy clays or highly siliceous fire brick grog.

With reference to the effect of silica in the clay and grog, data submitted by Purdy¹ on the expansion and contraction of

¹ *Trans. Am. Ceram. Soc.*, 15, 499-522 (1913).

porcelain body mixtures, shows that the expansion and contraction of fired test pieces, heated to and cooled from 900°C , is the greater the higher the flint content, and that the rate of expansion and contraction between 650° and 500°C is much greater than during other stages and that the higher the flint content, the greater is the rate of expansion and contraction during this period. The limits of composition as employed in Purdy's investigation with bodies containing clay and flint was 20 per cent. clay, 80 per cent. flint and 90 per cent. clay and 10 per cent. flint. Purdy noted that the total expansion at 900°C of the high flint body is about $2\frac{1}{2}$ times that of the high clay body and that the rate of expansion and contraction between 600° and 500°C of the high flint body is about 7 times as great as the high clay body, and for temperatures below 500°C about 3 times as great. Data obtained in the same way by Boeck,¹ on fired test pieces of fire clay and ball clay, shows that the expansion and contraction curve for fire clay has the same general trend as the porcelain bodies containing flint in Purdy's investigation, but the ball clay has a comparatively uniform rate of expansion and contraction between 900° and 200°C .

If, in cooling a high clay body, the contraction takes place at a uniform rate over a considerable temperature range, the body becomes more sensitive to strains as its rigidity increases, so that strains are more likely to occur at a dull red heat and after, than at the higher temperatures. When a body contains sandy clays, however, it not only has to contract more in cooling, but has to withstand the greatest rate of contraction during the period within which it is most sensitive to cooling strains.

Since it appears that the very dense, hard bodies are more sensitive to "dunting" than the more open porous ones and since it is common practice in manufacturing many clay wares to control the density, either wholly or in part by the introduction of sandy clays, it is suggested that the density of terra cotta bodies be controlled as far as possible by the size and amount of the grog, rather than by the use of sandy clays. It is further suggested that the cooling be conducted slowly below 650°C .

¹ *Trans. Am. Ceram. Soc.*, 14, 470-479 (1912).

While the method and rate of cooling is of the greatest importance in preventing "dunting," and terra cotta bodies of almost any density or composition will be free from dunting if cooled slowly enough, it is possible that, with the ordinary rate of cooling, in attempting to compound a body with low absorption, high crushing strength, and which will stand up best in the artificial freezing test, we might arrive at one that would be quite sensitive to "dunting"—particularly when manufactured into large pieces which are exposed on all sides to the action of the weather.

In order to manufacture terra cotta with straight and true lines it is essential that the body have as low a drying and burning shrinkage as possible, and that there be no tendency to warp in firing. These requirements are met with a body having a somewhat open, porous structure, rather than one which is hard and dense.

The body for terra cotta should have a reasonably low absorption, high crushing strength and stand up reasonably well in the artificial freezing test, but it is not advisable to go beyond this on account of the increased shrinkage, tendency to warp in firing, and sensitiveness to "dunting." In order to secure these desired properties I do not believe that it is necessary to develop a body which is able to withstand 30 of the sodium sulphate tests.

R. H. MINTON: Mr. Swalm admits my contention that the "character" of the grog and clays used is a more important factor in producing "dunting" than any other. This particularly applies to sandy grog or clays. His objection to the use of vitrified grog—owing to the difficulty of bonding with the plastic clays, is not sustained, as many terra cotta manufacturers have used vitrified grog entirely for certain purposes, and other manufacturers use it in large quantities. I have not experienced this difficulty in using vitrified grog, and even so, it would not arise in the use of the slag which does not have the smooth, clean surfaces of the porcelain and stoneware grogs.

It is perhaps unfortunate that my conclusions were based upon the disintegration and crushing strength data, but it is not clear

what other tests could have been used—as those employed are most conclusive in the determination of the weather-resisting qualities of any clay product.

Mr. Hill states that “the failure of terra cotta from ‘dunting’ is due to the inability to withstand changes of temperature—involving the expansion and contraction of the piece—and not to its inability to withstand disintegration or flaking due to the destructive action of freezing and thawing.” Mr. Hill has not proven that “dunting,” which develops in the wall, is not produced by the destructive action of freezing and thawing, regardless of what may be the primary cause. However, it was not intended to attempt to produce actual “dunting” by the freezing tests. These tests and the crushing tests were applied because they appeared to be best adapted to a measurement of the resistance of clay bodies to weathering action.

Mr. Hill further states that “terra cotta bodies giving the best results in the artificial freezing tests are those that are hard and dense and having a comparatively low absorption and high compressive strength; a body of this kind would, in all probability, be more sensitive to ‘dunting’ than one less dense and having a correspondingly higher absorption and lower strength.” Mr. Hill seems to overlook the real point at issue. The use of slag, or vitrified grog, does not necessarily produce a denser body so far as the clay matrix is concerned. The absorption is lowered merely because the slag grog has a lower absorption than the porous sagger grog. One of the terra cotta manufacturers has for many years used vitrified chemical stoneware or electrical porcelain grog in the manufacture of terra cotta which he supplies to a Canadian customer. Another manufacturer considered the use of common stoneware for the same purpose.

Mr. Hill also states: “it appears that the hard, dense bodies are more sensitive to fire-cracks than the others as are also those containing very sandy clays or highly silicious fire brick grog.” And again: “since the very dense, hard bodies seem more sensitive to ‘dunting’ than the more open porous ones, and since it is a common practice in the manufacture of many clay wares to control the density, either wholly or in part by the introduction of sandy clays, it is suggested that the density of terra cotta

bodies be controlled as far as possible by a variation in the size of the grog, rather than by the use of sandy clays."

In his original paper on "dunting" he states: "it has been noted that the bodies containing sandy clays are more sensitive to fire cracking than those made up of the more plastic clays." Also: "fire cracking seems to depend almost entirely on two factors, namely, the composition of the body and the rate and method of cooling. Regarding the composition, it was noted that bodies composed of very sandy clays are much more sensitive to fire cracking than those made of less sandy, more plastic clays." These statements seem to be contradictory.

My contention is that the "dunting" and failure of the terracotta is dependent more upon the "character" or "quality" of the grog and clays than upon the other factors and that a grog of low absorption is superior to the porous sagger grog. So far as price, weight, availability, working properties, etc., are concerned, it would appear that the slag is to be preferred to the grogs prepared from porcelain, stoneware, etc.

THE EFFECT OF ELECTROLYTES ON SOME PROPERTIES OF CLAYS.¹

By H. G. SCHURECHT, Columbus, Ohio.

Introduction.

One of the sources of loss in the manufacture of clay products, especially of the larger kind, chemical stoneware, glass pots, etc., is due to the lack of strength of the clays in the dry state and at the burning temperatures. Sufficient strength to resist the shocks and strains of handling in the green state is necessary. At certain periods in the burning the ware loses strength and is liable to warp, crack, or break, causing large kiln losses. The natural remedy would be to improve the strength of the clay body by artificial means or to introduce stronger clays.

The effect of the addition of organic compounds to clays has been studied by Acheson,² Minton³, Seger and Cramer,⁴ and Koerner,⁵ and it has been shown that the strength of the clays can be increased by the addition of gallo-tannic acid, catechu, straw emulsion, dextrine, or starch.

The effect of the addition of alkalies and acids on the volume shrinkages of clays in the plastic state has been reported by Bleining and Fulton,⁶ and Kerr and Fulton,⁷ but our information as to the effect of these electrolytes on the strength of clays is meagre. Bleining⁸ has reported that cast bodies containing alkalies may be stronger than bodies not containing alkalies. The writer⁹ has noted that the rate of disintegration in water is much slower for the deflocculated than for the flocculated clays.

¹ By permission of the Director, Bureau of Mines.

² *Trans. Am. Ceram. Soc.*, **6**, 31-64 (1904).

³ *Ibid.*, **6**, 231-259 (1904).

⁴ *Wein und Leipzig, A. Hartleben's Verlag*, **1909**, p. 82.

⁵ *Op. cit.*, pp. 82-84.

⁶ *Trans. Am. Ceram. Soc.*, **14**, 827-839 (1912).

⁷ *Ibid.*, **15**, 184-192 (1913).

⁸ Bureau of Standards, *Tech. Paper* **51**, 40 (1915).

⁹ *Trans. Am. Ceram. Soc.*, **19**, 144 (1917).

As the rate of its disintegration is sometimes used as a rough indication of the bonding power of a clay, further investigations with a view to studying the effect of the addition of alkalies and acids on the strengths of clays were carried out. A surprising increase in strength was gained by the addition of the alkalies, in some cases the strength of the treated clays being four times as great as that of the untreated. The present investigation was limited to a study of the effect of the addition of alkalies and acids on the properties of clays with special reference to their strength.

Method of Testing.—For the investigation the following mixtures were selected:

- (1) 50 parts Kentucky ball clay and 50 parts flint.
- (2) 50 parts Tenn. ball clay and 50 parts flint.
- (3) 50 parts Georgia kaolin and 50 parts flint.
- (4) 50 parts Kentucky ball clay and 50 parts grog.
- (5) 100 parts Kentucky ball clay.

The cross-breaking strength, water of plasticity, drying shrinkage, density and porosity were determined for each clay in the raw condition. The tests were made on the untreated clays and on the clays to which 0.05, 0.10, 0.15, 0.20, 0.40, 0.60, 0.80, 1.00, 1.50, 2.00, 3.00 and 5.00 per cent. (by weight) of electrolyte had been added. The electrolytes added were sodium hydroxide, sodium silicate, sodium carbonate, calcium hydroxide, tannic acid, and sulphuric acid.

Tests of the Clays in the Raw Condition.—For the cross-breaking tests, bars 1" x 1" x 7" were molded and dried at room temperature for 3 days, then in a drying oven at 65° C for 24 hours, and finally in the oven at 110° C for 24 hours. A span of 5 inches was used in breaking the pieces transversely. The modulus of rupture of each piece was calculated—the average of ten determinations being taken as the final result.

In making the water of plasticity and the drying shrinkage determinations, the electrolyte was added to a quantity of water slightly less than that required for developing the maximum plasticity. In case the limits for the normal consistency were large, the water was added by volume so as to keep the per cent.

added as nearly as possible the same, thereby making the shrinkage data more comparable.

The drying shrinkage was determined by the use of the kerosene immersion method and the per cent. volume shrinkages were calculated on the basis of the dry volumes.

The per cent. shrinkage in terms of the true clay volume was determined by the method described by Bleining¹ as follows:

$$s = \frac{d(v_1 - v_2)}{w} 100.$$

s = per cent. volume shrinkage in terms of the true clay volume.

d = specific gravity of the powdered clay.

v_1 = volume of the clay briquette in the wet condition.

v_2 = volume of the clay briquette in the dried condition.

w = weight of the dried briquette.

Tests of the Clays after Burning.—The test pieces were burned to cone 01 in a gas-fired test kiln, the temperature being increased at the rate of 30° C per hour from 1000° C to within 20° C. of the finishing temperature—at which point the rate was reduced to 10° C per hour. The apparent porosity, volume shrinkage, and density of each briquette was determined.

The cross-breaking tests were made on 4" × 0.8" × 0.8" bars, using a span of 3.2".

Effect of the Electrolytes on the Properties of the Clays and Mixtures.

Dry Strength.—In Figs. 1 and 2 is shown the effect of the addition of the electrolytes on the dry strength of the clays and mixtures studied. The addition of the alkalis and tannic acid to the clays increased the strength while the addition of sulphuric acid decreased the strength. Calcium hydroxide, when added in small quantities (0.2 to 2.0 per cent.), improves the strength somewhat but weakens the bodies when added in larger amounts. The maximum effect is produced by the addition of from 0.8 to 2.5 per cent. of the alkalis, or about 3.0 per cent. of tannic acid.

¹ Bureau of Standards, *Tech. Paper* 1, 21 (1910).

When caustic soda was added the bodies were molded with some difficulty and would not retain their shape unless a low per cent.

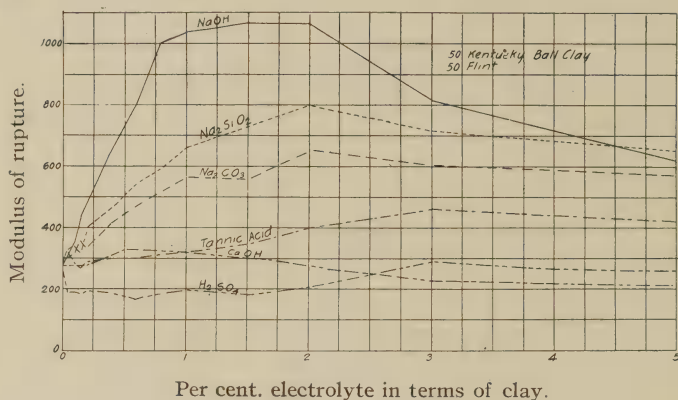


FIG. 1.—Dry Strength.

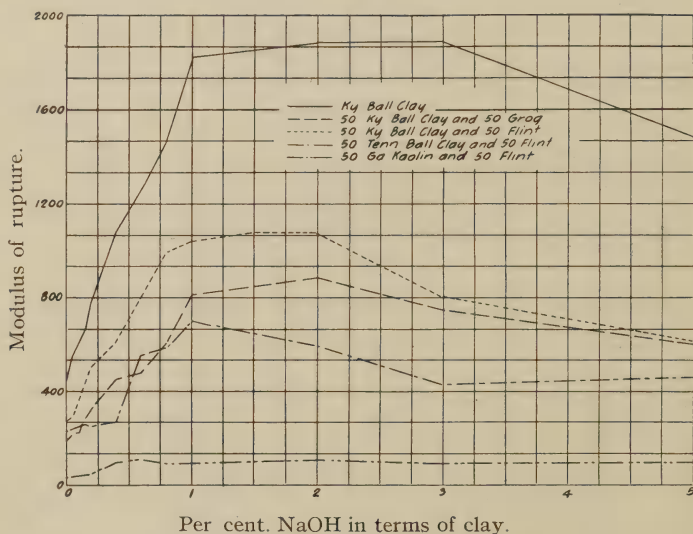


FIG. 2.—Dry Strength.

of water was employed, although in this condition the clays laminated badly. This effect was most pronounced in the mixtures

developing the greatest strength (see Fig. 1). The addition of sodium silicate, sodium carbonate, or more than 2 per cent. of sulphuric acid, affected the molding properties to a smaller extent and the addition of calcium hydroxide or tannic acid had little effect on the molding properties. The addition of less than 2.0 per cent. sulphuric acid was found to improve the working properties of a body.

The natural brown color of the ball clays changed to black upon the addition of a large percentage of alkalis or acids. The use of calcium hydroxide did not materially affect the natural coloring of the clays although it did cause the formation of flaky scales on the surfaces of the test pieces.

Under the microscope the clays treated with the alkalis appeared to be very fine grained, indicating that the clay substance present was in a deflocculated condition.

Water of Plasticity.—The curves in Figs. 3 and 4 show the effect of the electrolytes on the per cent. water of plasticity. In the case of the two ball clays the addition of the alkalis decreases

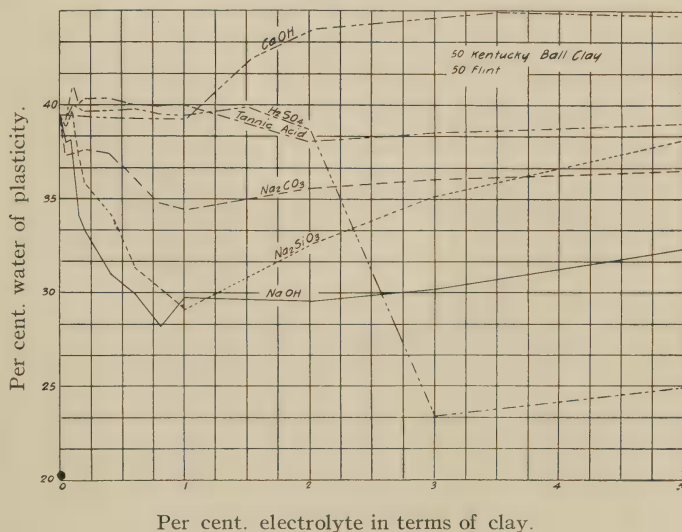


FIG. 3.—Water of Plasticity.

the per cent. water necessary to the development of the plasticity. The addition of a small amount of acid necessitates the use of a greater amount of water in working the clays but, if large quantities are added, a smaller amount of water must be used. The addition of calcium hydroxide increases the per cent. water of plasticity.

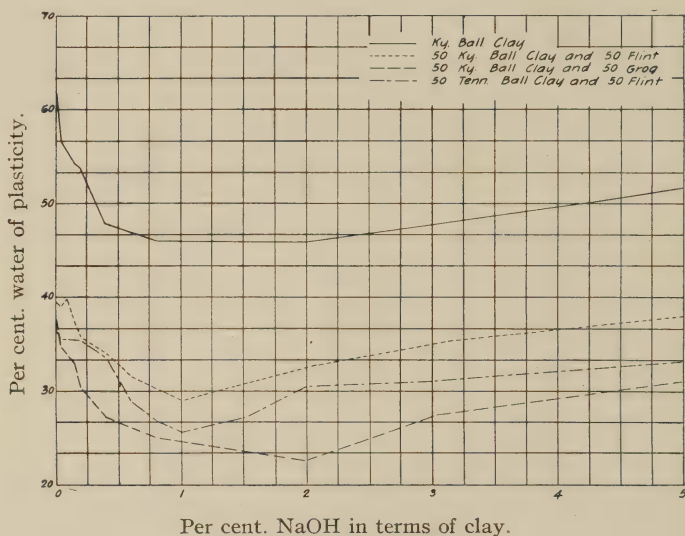


FIG. 4.—Water of Plasticity.

Volume Shrinkage.—In Figs. 5, 6 and 7 is shown the effect of the electrolytes on the volume shrinkages of the clays and mixtures. The addition of one per cent. of alkalis appears to decrease the volume shrinkage of the mixtures of 50 parts clay and 50 parts flint with the exception of the one containing Georgia kaolin, the shrinkage of this mixture being increased. The addition of sodium hydroxide to the Kentucky ball clay increases the shrinkage. Small percentages of sulphuric acid increase and large percentages decrease the volume shrinkages. The addition of calcium hydroxide and tannic acid increases the volume shrinkage.

The ratio of pore to shrinkage water becomes lower as the per

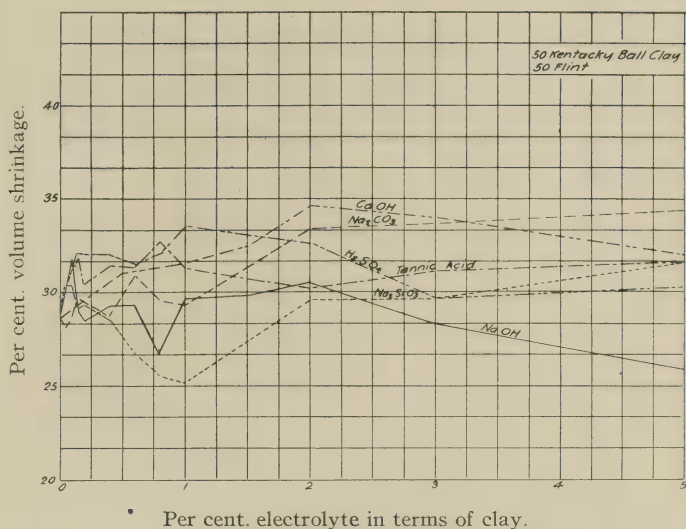


FIG. 5.—Volume Shrinkage.

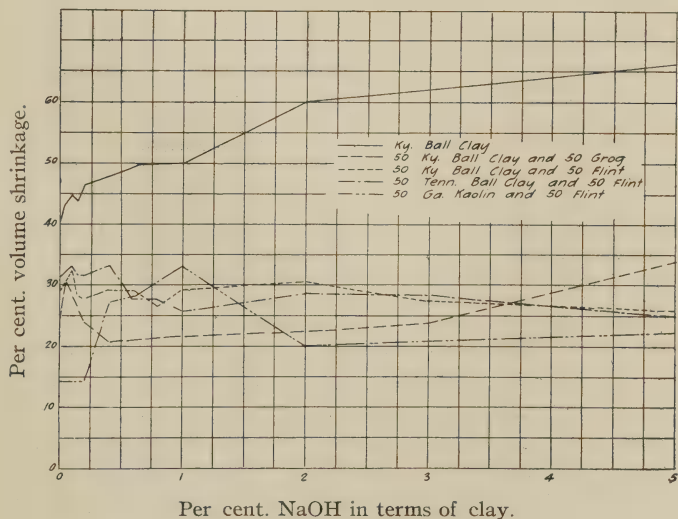


FIG. 6.—Volume Shrinkage.

cent. of shrinkage water in terms of the total water increases until 2.0 per cent. of caustic soda has been added when the reverse is true. As clays having a low pore to shrinkage water ratio and a high per cent. of shrinkage water in terms of the total water often developed good strength, these results are in accordance with the strength data. (See Fig. 1.)

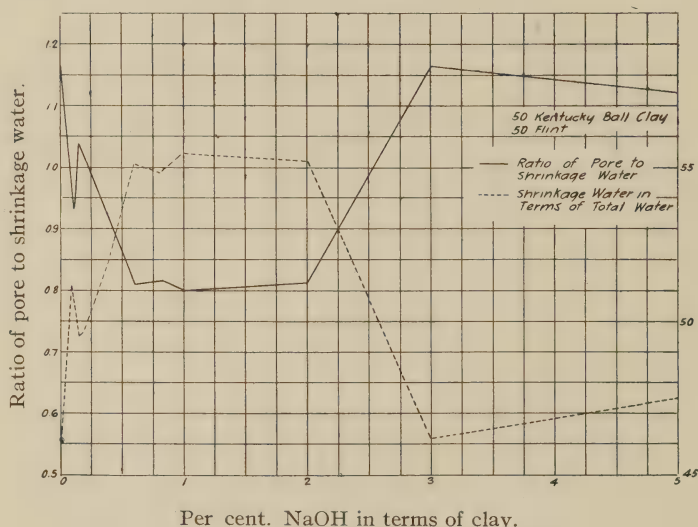


FIG. 7.—Shrinkage and Pore Water Relation.

Density.—In Figs. 8 and 9 are shown the effect of the electrolytes on the densities of the clays and mixtures. The alkalis and tannic acid increase the densities of the bodies, the maximum effect being produced by the addition of from 0.40 to 3.0 per cent. When more than 2.0 per cent. sulphuric acid is used the density is increased to a remarkable extent. However, there is only a small increase in strength (see Fig. 1), which may be accounted for by the oxidizing effect of the sulphuric acid and the consequent destruction of the organic bond. Additions of calcium hydroxide up to 1.0 per cent. increases the density. The addition of larger amounts decreases the density.

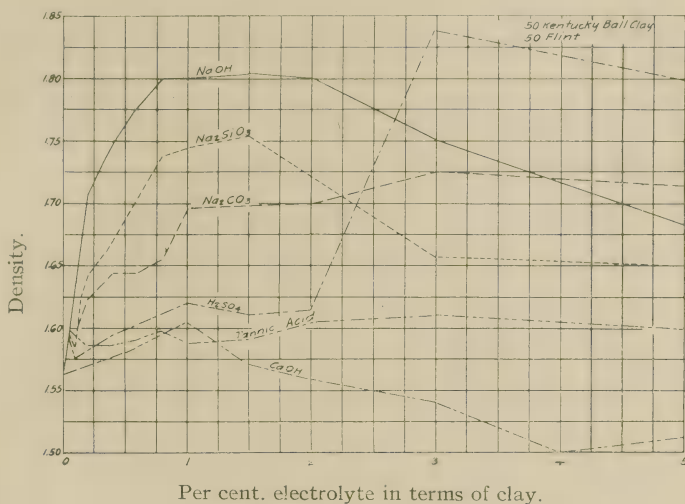


FIG. 8.—Dry Density.

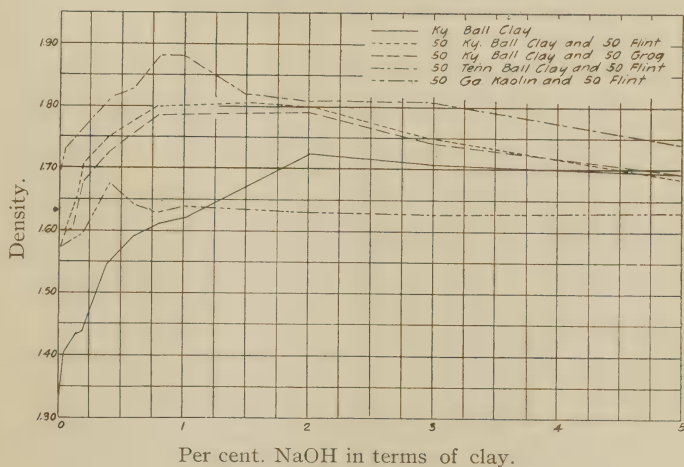


FIG. 9.—Dry Density.

Porosity.—In Figs. 10 and 11 are shown the effect of the electrolytes on the porosities of the clays in the dry condition. The porosity is decreased by the addition of the alkalis while the ad-

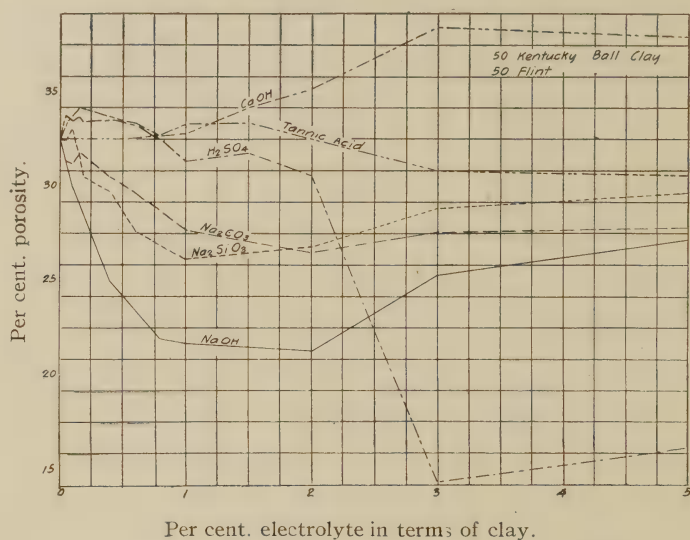


FIG. 10.—Dry Porosity.

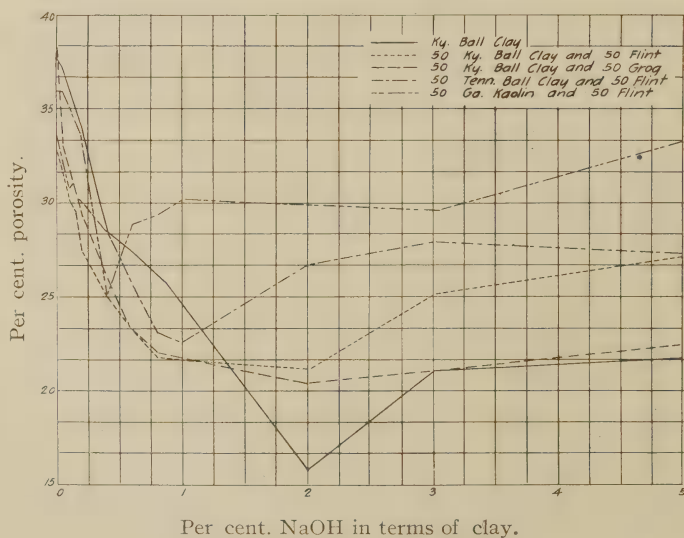


FIG. 11.—Dry Porosity.

dition of the acids in small percentages increases and in large percentages decreases the porosity. The porosity is increased by the addition of sodium hydroxide.

Burning Properties.—In Fig. 12 is shown the effect of sodium

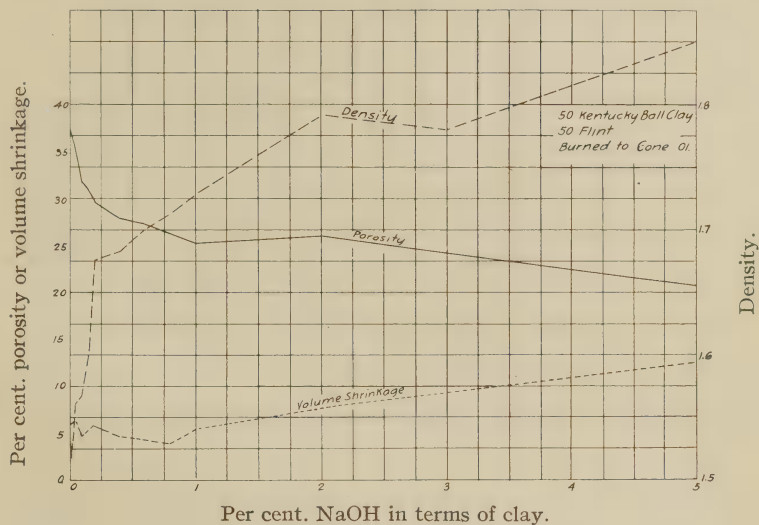


FIG. 12.—Burning Properties.

hydroxide on the burning properties of the mixture of 50 parts of Kentucky ball clay and 50 parts of flint when burned to cone 01. The volume shrinkage decreases with the addition of small quantities, up to 0.8 per cent., and is increased by the addition of larger amounts. The density is increased and the porosity decreased by the use of the sodium hydroxide. Considerable scumming and surface vitrification is noted with the addition of large percentages of sodium hydroxide.

In Fig. 13 is shown the effect of the electrolytes on the strength of the mixtures when burned to cone 8. Although the fluxing action of the alkalis increases the strength, there is a decided similarity between the burned and the raw strength data (see Fig. 1). In the burned condition, the maximum effect is pro-

duced by the alkalis when from 0.8 to 2.5 per cent. is added—the caustic soda being the most effective.

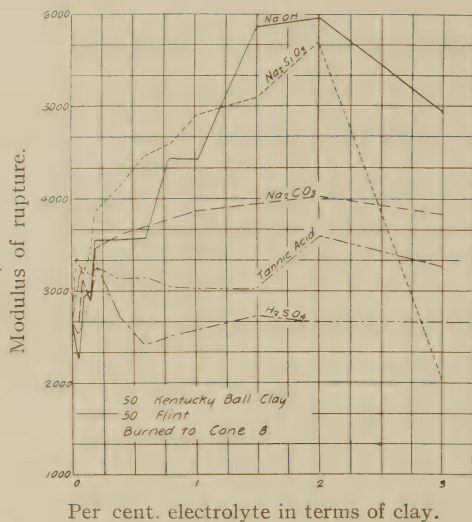


FIG. 13.—Burned Strength.

Summary.

The strength of clays when dry may be increased by the addition of the following electrolytes to the bodies in the plastic state, the first named being the most effective: (1) sodium hydroxide, (2) sodium silicate, (3) sodium carbonate, (4) tannic acid, and (5) calcium hydroxide. The addition of sodium hydroxide increases the strength of some of the mixtures as much as 400 per cent. Small percentages of sulphuric acid decrease the strength of Kentucky ball clay. More than 2.0 per cent. of calcium hydroxide decreases the strength of Kentucky ball clay.

The addition of from 0.80 to 2.5 per cent. of caustic soda affects adversely the molding properties of the bodies, as evidenced by their inability to retain their shape when molded, unless a very low per cent. of water is used. This is also noticeable, to a lesser extent, with additions of sodium silicate, sodium carbonate, or more than 2.0 per cent. of sulphuric acid, but is not so notice-

able with additions of calcium hydroxide or tannic acid. The addition of less than 2.0 per cent. of sulphuric acid improves the molding properties of the bodies.

In the case of the two ball clays, the addition of the alkalies lowers the per cent. water of plasticity. The addition of the acids at first increases and then decreases the water required for working the bodies. The addition of calcium hydroxide increases the water of plasticity.

The addition of from 1.0 to 2.0 per cent. of alkalies decreases the volume shrinkages of the 50 parts clay and 50 part flint mixtures with the exception of the one in which Georgia kaolin is used, in this case, the shrinkage being increased. The addition of sodium hydroxide to Kentucky ball clay increases its shrinkage. Sulphuric acid, in small percentages, increases the shrinkage and in larger percentages decreases the shrinkage. Tannic acid and calcium hydroxide increase the shrinkage.

The addition of alkalies and acids increases the densities of the clays and mixtures when dry. In amounts up to 1.0 per cent. calcium hydroxide increases the density. The addition of larger amounts decreases the density.

The porosity is lowered by the addition of alkalies and increased by the addition of acids in small percentages. Large additions of acids are accompanied by decreases in porosity. Calcium hydroxide increases the porosity.

The burning shrinkage at cone 01 is lowered by the addition of small percentages of caustic soda and is increased by the addition of larger quantities. The addition of sodium hydroxide increases the density and decreases the porosity in the burned condition.

The addition of the following electrolytes to the bodies in the plastic condition increases the strength of pieces burned to cone 8, the most effective being named first: (1) sodium hydroxide, (2) sodium silicate, (3) sodium carbonate, and (4) tannic acid.

Discussion.

MR. WHITAKER: I would like to ask Mr. Schurecht what effect ageing would have on the strength of the bodies to which

the electrolytes have been added? Would ageing still further increase the strength?

MR. SCHURECHT: We have not determined the effect of ageing on the strength of the clays, although we have determined the effect of the ageing of clay slips to which electrolytes have been added and found that it changes the viscosity. The ageing undoubtedly has an effect upon some of the other properties of the clays.

PROF. STALEY: It would appear that one of the chief advantages in having a clay of good strength would be that we might expect less cracking during drying. Several years ago, I did some work on "The Effect of the Addition of Salts on the Drying Properties of Clays."¹ In this I noted that the addition of the alkalies invariably increased the tendency of the clays to crack in drying. Possibly the pieces of very carefully dried ware, free from cracks, would have shown high strength, as in the case of Mr. Schurecht's samples, but it does not appear to be good practice to increase the possible strength of a clay by the addition of alkalies, if these additions are going to introduce drying difficulties, which make it very difficult to obtain sound ware in ordinary factory practice.

In my work, I have found that the introduction of small amounts of acid and neutral salts decreased the tendency to cracking.

MR. SHAW: My experience in the use of electrolytes in the casting of bodies bears out that of Mr. Staley. The tendency to crack was very great. I should add, however, that the plastic clays which I used were of very low grade.

COMMUNICATED DISCUSSION.

W. W. GREENWOOD: Mr. Schurecht's paper presents material which is of interest to the chemist as well as to the ceramist. In dealing with so complex a subject as the chemistry of electrolytes, great care of manipulation is essential if the results of the work are to be of much value. In this particular piece of work the writer shows such care and has handled the necessary details

¹ *Trans. Am. Ceram. Soc.*, 17, 697-711 (1915).

of his experiments with a thoroughness which makes one feel like accepting his observations as authentic.

It would have been helpful, however, if in this paper the author could have gone a little more into detail as to the theory of his subject or if he had speculated as to why the phenomena which he observed occur. This is of value for two reasons: first, because in most cases the experimenter is better able to correlate his work with existing information—he being more familiar with the subject than the outsider; second (and this applies to the case at hand), because by not doing this Mr. Schurecht leaves the reader in a position where he may draw wrong conclusions from the facts presented.

In his summary, he states: "The dry strength may be increased by adding the following electrolytes to the bodies in the plastic state, those which are most effective being named first: (1) sodium hydroxide, (2) sodium silicate, (3) sodium carbonate, (4) tannic acid, and (5) calcium hydroxide." There is danger in assuming from this statement that the electrolytes mentioned were directly responsible for the increased strength of the dried bodies. There is nothing in the observations presented to uphold this theory. In fact, it would seem quite probable that the electrolytes are only indirectly responsible for this action. We know that their addition deflocculated the clays and the statement is made in the paper that "under the microscope it could be seen that the clays treated with alkalis consisted of very fine grains, a characteristic of deflocculated clays, while the untreated clay is much coarser." Does it not seem reasonable that the increased strength observed was at least partially due to the fineness of the particles in the treated clays? These finer particles would tend to pack closer together and consequently there would be fewer voids than in the untreated clays. In other words, this resulting strength is of mechanical origin brought about by chemical means. If such is the case—and there is much in the paper which points in this direction—the electrolytic action is simply a means towards an end—a method if you please of obtaining fine particles of clay compacted together which in turn produce greater mechanical strength.

In another part of his summary the statement is made: "The strength after being burned to cone 8 may be increased by adding the following electrolytes to the bodies in the plastic state, those which are most effective being named first: (1) sodium hydroxide (2) sodium silicate, (3) sodium carbonate, and (4) tannic acid."

Here again there is a chance for difference of opinion as to the cause of this increased strength. No doubt it is of chemical origin, but there is nothing in the paper to show whether the reagents named produced it because they were electrolytes or because of their alkali content. Binns,¹ in discussing the action of tannins on clays, notes that alkaline salts in the tannins would become operative at the higher temperatures.

How would one of these treated clays, when dry, differ from an untreated sample? Would there not be minute particles of alkaline salts about each grain? When the clay was burned these salts might be expected to exert a fluxing action and consequently a stronger and denser body would result. In the familiar process of "salt glazing," the alkali, freed from the decomposing sodium chloride, acts on the outside of the ware and glazes it—here the alkali would be in a position to act as a fluxing agent throughout the structure of the ware. So again the electrolytes themselves would be only indirectly responsible for the results noted.

The work of this paper indicates another bit of data which it would be worth while to determine. In two cases the order of effectiveness of these electrolytes is (1) sodium hydroxide, (2) sodium silicate, (3) sodium carbonate and (4) tannic acid. It would be of interest to know whether this is due to the characteristics of the reagents themselves or to their alkali content. In the two cases cited, the order of strength as electrolytes is directly proportional to the alkali content. Sodium carbonate would, in solution, hydrolyze and show a weak alkaline reaction; sodium silicate acts as a fairly strong alkali toward litmus—depending of course upon its concentration—and sodium hydrate is the strongest of all.

It may be possible that the whole theory of the effect of electrolytes on clays is really based upon the action of alkalies upon clays.

¹ *Trans. Am. Ceram. Soc.*, 6, 57 (1904).

JOURNAL

OF THE

AMERICAN CERAMIC SOCIETY

A monthly journal devoted to the arts and sciences related to the silicate industries.

Vol. 1

April, 1918

No. 4

EDITORIALS.

THE PRESENT UNUSUAL DEMAND FOR MEN WITH TECHNICAL CERAMIC TRAINING.

Probably the best known of the trite sayings of Andrew Carnegie is the admonition to "put all your eggs in one basket and watch that basket" but another which has enjoyed a very wide circulation is the advice given to a business friend which was, in substance, "If you have a hundred thousand dollars to spend on the development of a new proposition, spend the first fifty thousand in finding out what is already known."

Twenty years ago, or at about the time the American Ceramic Society was formed, it was in rare cases only that any systematic attempt was made to find out in advance of embarking upon a new proposition or of attempting to develop some new product or new manufacturing process, what successes or what failures had accompanied similar earlier experiences in attempting to accomplish the same or similar results and it was almost never that a systematic attempt was made to determine in advance what laws of nature, chemical or physical, were to be met with in carrying out the undertaking and what influences such laws must have in determining the limitations under which the work must be done.

Today the situation is very different. The evolution has been almost a revolution. The old methods of secrecy and distrust and ignorance have given way to frank discussion and to more than a beginning of real knowledge in the science of silicates. As an integral part of this evolution (or revolution) has come the

establishment and growth of departments in our institutions of learning devoted to the study of the fundamentals underlying all processes of silicate manufacturing and the dissemination throughout the industry of the knowledge thus accumulated.

This evolution has borne fruit abundantly. With it there has come an ever-increasing demand for men with suitable training, capable of taking their places in the manufacturing industries. This demand is felt in all branches of the silicate industries—in the clayware industries, in glass plants, in cement mills, in enameling plants and in the many allied manufacturing establishments.

With this logical development of the industry along normal lines has come the added stimulus of war demands. One feature of the very unusual situation created by the world war is the necessity that has arisen in many branches of the Ceramic Industries, in common with almost all other manufacturing industries, of replacing with materials of domestic origin or of domestic manufacture, materials which were formerly imported. Such importations have been cut off either because imported articles formerly came from the enemy countries or because the great demand for shipping facilities for purely war purposes has made it impossible to continue shipments of materials which could be duplicated at home. It has taken a tremendous amount of investigation and research, both theoretical and practical, to accomplish the substitution of suitable domestic materials for the former imported articles.

Another special demand upon the Ceramic industries is that for new products and improved forms and qualities of old products made necessary by the new demands of a war business. The Nation's business is, and has been for a year and a half, the business of War and products demanded by the new manufactures incident thereto have had to be made. New knowledge and new experience have been most essential in meeting the new difficulties involved.

With a careful analysis of the situation at hand, it is not difficult to understand the present great demand for men trained in the sciences upon which the silicate industries are founded. Our institutions of learning report very heavy demands for men, and these demands they are quite unable to satisfy with the com-

paratively small number of men undergoing such training. From the larger public and private laboratories interested in the silicate work come the same reports of numerous demands for trained men. The demand far exceeds the supply. It cannot be denied that this situation of heavy demand and limited supply has been responsible for the fact that training has not always been as complete as it should have been, but very great strides have been made, within the past decade especially.

The calling is one offering a very attractive future in the interesting nature of the work, in the possibilities of development, and in remuneration and there can be no doubt that in proportion to the increase in a general realization of this situation will come an increase in the number of young men who fit themselves to supply this demand by entering our colleges and universities to gain the required training in the scientific courses dealing with ceramic work.

AMERICAN CERAMIC SOCIETY AT THE FOURTH NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES.

The American Ceramic Society will be represented at the Fourth National Exposition of Chemical Industries to be held at the Grand Central Palace, New York City, the week of Sept. 23rd.

The participation of the Society in the Exposition of last year evidenced an unusual interest in ceramic work and this year the Exposition management has arranged for the grouping of the ceramic exhibits in a Ceramic Section. The American Ceramic Society will have its headquarters in this Section.

The Ceramic industry includes that branch of the chemical industry engaged in the production and manufacture of silicates. Including as it does a group of industries producing materials and wares to the value of hundreds of millions of dollars, it is one of the largest single branches of manufacture based upon chemical technology.

Although the public at large has perhaps appreciated the recent progress made in other branches of the chemical industry,

such as in the manufacture of dyes and munitions, it does not have a thorough realization of the extent of the ceramic industries nor of their basic importance to the so-called "essential industries." The war essential nature of some of the products which are being produced by this group of manufacturers should also not be overlooked.

Among the ceramic products which are vitally necessary to the successful manufacture of other essential products we would mention fire brick, furnace linings, flue linings, crucibles, retorts and other REFRACTORIES used in the production of iron, steel, brass, copper and other metals and their alloys; ABRASIVES for the grinding of optical products, munitions, machine parts, etc.; CHEMICAL PORCELAIN AND STONEWARE for the production of acids, heavy chemicals, explosives, etc. PORTLAND CEMENT for ships, building construction, etc.; BUILDING AND CONSTRUCTION MATERIALS as brick, tile, fire-proofing, terra cotta, conduits, sewer pipe, drain tile, etc., necessary for the construction of Government buildings, ordnance storehouses, training camps, etc.; and ENAMELED IRON WARE used in the manufacture of chemicals, explosive products, etc., and very extensively for the serving of food in both the Army and Navy.

The Ceramic Industry has also been called upon to develop and produce certain military products of a vitally essential nature and which were imported into this country previous to the war. Among these should be mentioned OPTICAL GLASS for gun sights, range finders, periscopes, etc.; SPECIAL GLASS for searchlight reflectors, ships' lights, etc.; SPARK PLUGS for airplane engines; IMPROVED REFRACTORIES for the furnaces of destroyers and other battle craft; and LABORATORY GLASSWARE AND PORCELAIN for experimental and control work in the chemical industries.

The Ceramic Section at the coming Fourth National Exposition of Chemical Industries will undoubtedly awaken the interest—not only of those engaged in the production of ceramic wares—but also of many of the engineers, chemists, superintendents and others in attendance and in whose work important use is made of Ceramic products.

ORIGINAL PAPERS AND DISCUSSIONS.

THE EFFECT OF THE DEGREE OF SMELTING ON THE PROPERTIES OF A FRIT.

By E. P. POSTE AND B. A. RICE, Elyria, Ohio.

Introduction.

In a consideration of the actual composition of a frit, we assume that certain constituents entering into the raw mixture pass through chemical changes which bring about the volatilization of certain portions and the fusing together of the remaining ingredients into a homogeneous mass having a certain definite chemical composition. This we express in terms of the melted oxides or by means of the molecular formula. Not only is this assumption made relative to the enamel frits, but it also finds application in connection with fritted glazes, glasses and various other ceramic products which result from the use of mixtures of such materials as soda, feldspar, borax, fluorspar, etc.

Upon reading the literature on the subject of the chemistry of frits, we find that the above general conditions are taken for granted; we do not find a report of an investigation leading to a comparison between the actual composition of the resulting frit and the theoretical composition as shown by the computed formula.

If we assume that, at some particular stage in the smelting of an enamel, the actual composition corresponds to the theoretical composition, there must be two stages, one on either side of this particular point, during the first of which there are still present some of the materials which are volatile in the ordinary sense of the term, and beyond which point further heating may possibly cause decomposition and volatilization of some of those materials which we ordinarily consider as being non-volatile.

Some months ago, a series of experiments was started which has thrown considerable light on this particular subject and the results may be of sufficient interest to others engaged in the ceramic industries to warrant the presentation of this paper.

Experimental.

The work has included the melting of a commercial enamel formula under conditions covering a large variation in the time of smelting. The enamel thus produced has been studied, not as to its behavior when applied to the ware, but as to the chemical and physical changes which have been brought about by the different degrees of smelting. Samples of each have been analyzed and the results compared with the theoretical composition of the frit. Deformation tests have been made in order to determine the effect of the various degrees of smelting upon the deformation behavior of the resulting frit. Tests to determine the effect of the varying heat treatments on the resistance of the enamels to acids have also been made.

As to the formula used, it will be sufficient to state that it was fairly resistant to acids and prepared from the usual enamel constituents. We can draw definite conclusions in a relative manner without stating the formula of the enamel or the actual analyses of the resulting frits.

The raw materials, properly mixed, were placed in a tilting smelter which had been pre-heated in the usual manner. As soon as the material had reached a fairly uniform condition of fusion and after thorough stirring, a small portion of the enamel was withdrawn from the smelter—the total time required to reach this condition being taken as unity. This enamel was designated as "A." In like manner samples were poured from the smelter at the following time intervals based on the former as unity: $1\frac{1}{2}$, 2, $2\frac{1}{2}$, 3 and $3\frac{1}{2}$, the samples being designated A, B, C, D, E and F, respectively.

The samples thus prepared were thoroughly dried and uniformly ground dry, without mill additions, in an experimental pebble mill. That portion of the resulting powder passing a 200-mesh sieve was used as the basis of the three following tests:

1. Chemical Analyses.

The chemical analyses of the six samples were made in the usual manner. The scheme outlined by Landrum¹ proved very helpful in this work. Mellor's Treatise on the Ceramic Industries, Vol. 1, proved a most reliable guide.

2. Deformation Test.

A portion of the 200-mesh powder was mixed with water and an organic binder and molded into test cones of standard dimensions. The cones were thoroughly dried and mounted in pairs on a piece of asbestos board. This mounting was placed in an electric furnace (at a temperature of 600° F.) in such a manner that the junction of a thermocouple was just between the two cones. The temperature of the furnace was gradually increased at a uniform rate and two points noted. The first of these was the temperature at which the tip of the cone was first observed to move and the second, the temperature at which the tip of the cone was just touching the asbestos board upon which the cones were mounted. By noting both cones in this manner and taking the average temperature at which they were first observed to deform and at which they were touching, two readings were obtained, the first of which was termed the starting point and the second, the deformation point. The term "Deformation range" has been applied to the interval existing between these two temperatures and has been considered as indicating the general range through which the enamel is in a semi-fused condition but still sufficiently viscous to remain in place.

3. Acid Test.

The acid test was made on the 200-mesh powder in accordance with the methods which have been previously worked out and reported.² The method in brief is as follows:

Two grams of the frit were carefully weighed in a 400 cc. beaker, to which was added 100 cc. of the desired solution (10 per cent. hydrochloric acid in this case).

¹ *Trans. Am. Ceram. Soc.*, 12, 144 (1910).

² *Ibid.*, 17, 137 (1915); 18, 570 (1916); 19, 146 (1917).

The contents of the beaker were thoroughly stirred, covered with a watch glass and then allowed to stand at the laboratory temperature for 24 hours. The remaining frit was then washed into a weighed Gooch crucible, all traces of acid removed, the crucible dried and weighed, and the loss of weight determined. This loss of weight was taken as the acid loss under these conditions. In this manner, by running a series of tests under parallel conditions, a very good comparison results. Obviously, the actual temperature has an effect on the results but under these particular conditions the results are comparative as the same temperature has existed during all of the tests.

Chemical Analyses: Results.

As to the actual analyses of the six samples—the first step was to determine whether fluorine was present in the frit as a considerable quantity of fluorspar had been used in the raw batches. Thorough qualitative tests did not detect the presence of fluorine. This fact is interesting in view of the statement made by Landrum¹—"In a ground coat enamel for sheet steel, where the frits are properly fused, the fluorine from the calcium fluoride entirely disappears. In white enamels, however, when cryolite is added as an opacifier, the melting is not carried so far and fluorine does remain in the enamel." The enamel in question contains no cryolite and the fluorine from the fluorspar was all volatilized—even in the first sample which had been smelted to a lesser degree than it would be in the production of an ordinary commercial frit from this formula.

An appreciation of the results of these analyses can be had by a consideration of the SiO_2 , Al_2O_3 , B_2O_3 , CaO , K_2O , and Na_2O contents. There were other ingredients present in small quantities in the enamels but their fluctuations throughout the series are not important.

In Table I we have taken the theoretical composition of the enamel as a standard and have indicated the excess or deficiency of SiO_2 , Al_2O_3 , B_2O_3 , CaO , K_2O and Na_2O as related to the theoretical amounts. For instance, in enamel "A" there was present

¹ *Trans. Am. Ceram. Soc.*, 14, 544 (1912).

3.88 per cent. less of SiO_2 than is called for in the theoretical formula while in "B," there was 0.46 per cent. more.

TABLE I.¹

	A.	B.	C.	D.	E.	F.
SiO_2	-3.88	+0.46	+1.32	+2.56	+4.62	+7.92
Al_2O_3	+0.51	+0.40	+0.50	+0.45	+0.62	+0.80
B_2O_3	-0.10	-1.80	-2.90	-3.20	-4.20	-6.00
CaO	+0.73	+0.52	+0.37	+0.35	+0.30	+0.17
K_2O	+1.63	+1.10	+1.00	+0.43	+0.40	+0.26
Na_2O	+1.18	+0.18	-1.22	-1.93	-2.50	-2.77

A graphical interpretation of these results is very interesting. In Fig. 1 we have considered the horizontal line at the center of the chart to indicate the actual determination corresponding

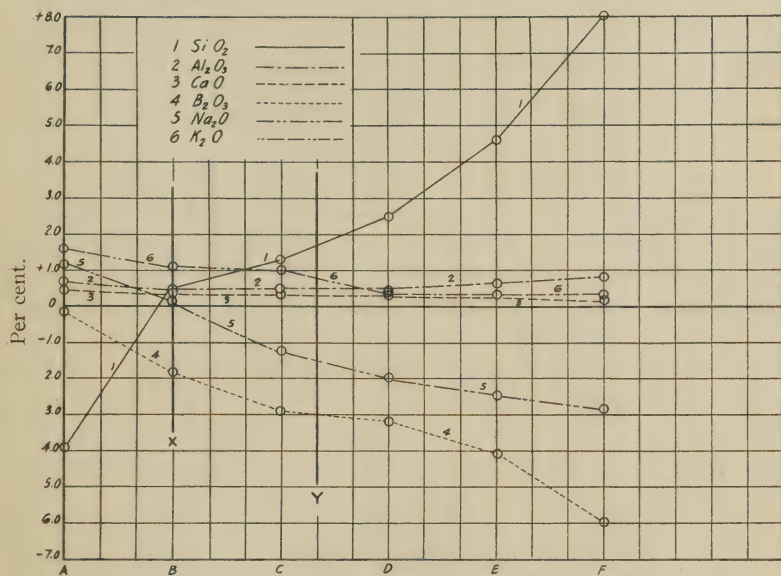


FIG. 1.

to the theoretical value. If the analysis value exceeds the theoretical amount, it has been designated by a position above the horizontal line, and if the figure has been below the theoretical

¹ In three cases the values here reported are slightly different from the analytical data—modified to be consistent with the balance of the data.

amount, it has been placed below the line. The horizontal distances AB, AC, AD, AE and AF, indicate the time of smelting of each of the respective samples, A being taken as unity.

A study of Fig. 1 leads to certain very definite conclusions. The changes prior to "A" cover the period during which the water is vaporized and most of the nitrates, carbonates and fluorides are decomposed. Beyond "A," a very definite series of changes of another type take place.

It will be seen that the increase in the time of heating has produced a very rapid increase in the percentage of SiO_2 up to "B," after which the rise is very positive but more gradual.

The Al_2O_3 content has not been subject to very marked changes. At "A," it was slightly above the theoretical amount and throughout the series it has at first dropped and then increased gradually and at "F" is somewhat above the value at "A."

The CaO content has slightly decreased from "A" to "F," although always being slightly above the theoretical amount.

The percentage of alkalis has dropped quite materially from "A" to "F" and it is particularly interesting to note that the volatilization of Na_2O has been much more rapid than that of K_2O . In fact, throughout the series there is more K_2O than the theoretical amount, while the Na_2O content drops below the theoretical shortly beyond "B" and at "F" there is a deficiency of nearly 3.0 per cent.

The B_2O_3 content is about equal to the theoretical at "A" and then drops off steadily to "F."

There appears to be a definite point at "B," at which the composition of the entire batch is nearest to that of the theoretical composition—in fact the algebraic sum of the values is practically zero. The line "X" has been drawn through this point on all of the charts. It would seem that the most radical changes, due to the volatilization of substances ordinarily considered as volatile, have come practically to equilibrium at this point. The water has been completely driven off, the nitrates decomposed, the carbonates broken down and the fluorine—with its equivalent of silica—has vaporized as silicon tetrafluoride. In addition to this there has been a noticeable loss in B_2O_3 —due to volatilization.

Beyond this line "X" the volatilization of B_2O_3 continues at about the same rate although there seems to be a radical change in the type of the curve for SiO_2 and Na_2O . It is quite apparent that the volatilization of the B_2O_3 and Na_2O is the determining factor in this change and that the increase in the SiO_2 content of the frit is the result.

It is further very interesting to note the point corresponding to the time at which this enamel would normally be poured. The line "Y" has been drawn through this point. We have the following values: $SiO_2 + 1.7$, $Al_2O_3 + 0.5$, $CaO + 0.3$, $K_2O + 1.9$, $Na_2O - 1.5$, and $B_2O_3 - 3.0$. In other words, the frit, as it would normally leave the smelter, is considerably higher in SiO_2 , somewhat higher in K_2O , Al_2O_3 and CaO , slightly lower in Na_2O , and very materially lower in B_2O_3 than would be indicated from the theoretical composition obtained from computation.

The data in Table 1 has been calculated on a percentage basis and as is characteristic of data of this kind—a change in the amount of any one constituent, when the actual amount of the others remains constant, makes a difference in the percentage values of the other constituents.

An effort has been made to present the analytical data in a form which will eliminate these objections (Table 2). In doing this we have assumed that, in view of the absence of fluorine in "A," the actual amount of SiO_2 left in the batch through the subsequent stages of the smelting is the same, and that the changes which have taken place have involved the volatilization of other substances.

TABLE 2.

	A.	B.	C.	D.	E.	F.
SiO_2	Assumed constant.					
Al_2O_3	0	-0.56	-0.56	-0.71	-0.73	-0.85
B_2O_3	0	-3.70	-4.95	-5.70	-7.22	-9.50
CaO	0	-0.57	-0.77	-0.89	-1.05	-1.34
K_2O	0	-1.01	-1.19	-1.80	-1.95	-2.31
Na_2O	0	-2.30	-3.73	-3.92	-5.55	-6.30

Assuming that in heating from A to B no change was made in the actual amount of SiO_2 , the values for the other oxides have been changed, keeping their ratio to the SiO_2 the same and bring-

ing the SiO_2 to the same actual amount as was indicated in "A." In view of the fact that the percentage of SiO_2 was constantly increasing from A to F, the assumption that the actual weight has been constant has caused a decrease in the actual amounts of the other oxides present. In columns B, C, D, E and F, the actual loss of Al_2O_3 , B_2O_3 , CaO , K_2O and Na_2O as compared with the actual amounts present in A has been expressed. For instance, in B, assuming that there was no loss of SiO_2 , the amount of B_2O_3 is 3.7 points less than was present in A.

In Fig. 2 the data of this table is presented graphically. The line at the top of the chart is designated as zero. The different times of smelting are indicated by A, B, C, D, E and F. The dis-

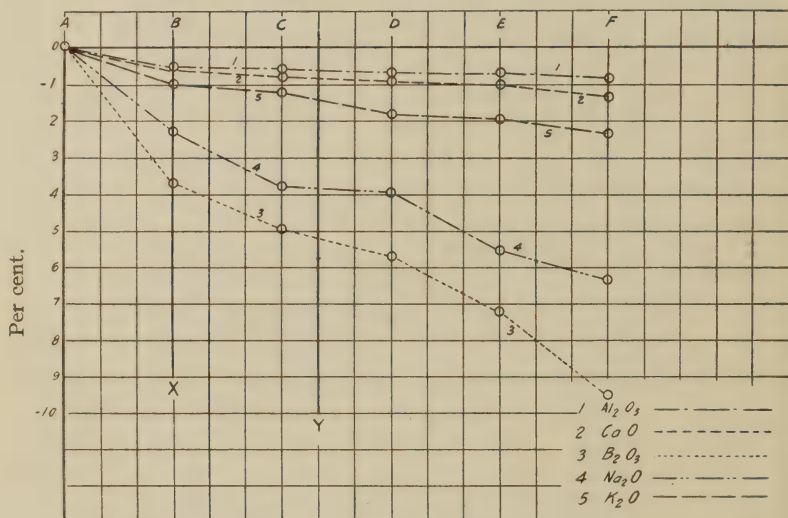


FIG. 2.

tance below the zero line indicates the loss in the amount of the various constituents as compared with the amounts present in A.

From Fig. 2 it will be evident that, on assuming a constant amount of SiO_2 from A on, there has been a gradual loss in the amount of CaO and Al_2O_3 , a greater loss in K_2O , and a very material loss in the amounts of Na_2O and B_2O_3 . The change in the

direction of the various curves at the line "X" is again quite noticeable.

The above data and curves would indicate that there is a loss of CaO and Al_2O_3 due to the continuous heating from A to F. If this condition is taken as improbable, the data could be rearranged, keeping either the content of CaO or Al_2O_3 constant, in which case the value for the SiO_2 would constantly increase. At the same time there would still be a definite decrease in the amount of B_2O_3 and the alkalis.

As a general conclusion, from the data presented from this point of view, it is quite clear that there is a very marked volatilization of the B_2O_3 and alkalis. Further than this there has been either an increase in the amount of SiO_2 or a decrease in the amount of CaO and Al_2O_3 . It hardly seems possible that an absorption of SiO_2 from the walls of the smelter could have taken place and no other source is possible. We therefore conclude that a slight volatilization of the other two oxides took place.

Results: Deformation Tests.

The results of the deformation tests which were made in accordance with the foregoing outline have been rearranged as shown in Table 3. The deformation temperature of A has been taken as a standard and the increase in the deformation temperature above this point is the figure which is given as the value for the deformation temperature of any particular enamel. The deformation range, as given, is the actual temperature interval occurring between the first perceptible tipping of the cone and the final touching of the tip of the cone at the base of the cone mounting.

TABLE 3.

	A.	B.	C.	D.	E.	F.
Deformation Temp..	0° F.	10° F.	30° F.	50° F.	60° F.	80° F.
Deformation Range...	60°	80°	110°	120°	140°	170°

The above figures are readily interpreted by the use of Fig. 3, which shows both the deformation temperatures of the enamels B, C, D, E and F, relative to the deformation temperature of A, and their actual deformation ranges.

A study of Fig. 3 throws some light on the effects of the chemical changes, as indicated by the analyses, upon the physical

properties of the enamels as indicated by the deformation points and deformation ranges. It will be noted that the curve for the deformation temperatures approximates a straight line which rises quite uniformly from A to F, the total increase in deforma-

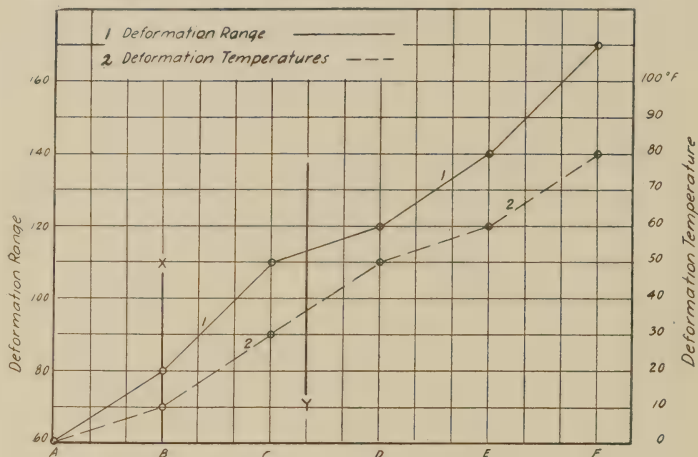


FIG. 3.

tion temperature being about 80° F. The curve for the deformation range is of a very similar nature, showing a range of 60° F. at A and about 170° F. at F.

The observations on both of these curves having been made to the nearest 10°, allowance of this amount for experimental error would make either of these curves very uniform.

There are two additional physical properties of the frit which it will be interesting to take into account. By drawing a hair of enamel from a batch during smelting there is a period during which the hair will contain particles of unfused material and will be quite brittle. As the mass reaches a quiet fusion, the brittleness of this hair greatly diminishes and finally a point of maximum toughness is reached, beyond which it again becomes brittle. For this particular enamel this point of maximum toughness would be crossed by the line "Y" in Fig. 1.

A further observation has to do with the coefficient of expansion of this particular enamel. The theoretical enamel has a coefficient

of linear expansion of 93.7×10^{-7} , calculated by the use of the factors given by Hovestadt.¹ The coefficients of expansion for A, B, C, D, E and F have been computed from the analytical data. These data are given in Table 4 and are plotted graphically in Fig. 4.

TABLE 4.
Coefficient of Linear Expansion.

Theoretical.....	A.	B.	C.	D.	E.	F.
93.7×10^{-7}	101.1	96.9	92.3	88.4	88.0	88.2

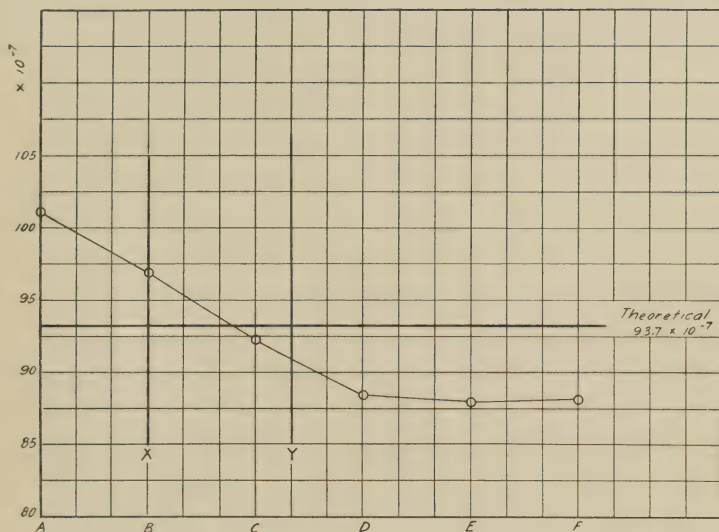


FIG. 4.—Coefficients of expansion.

Results: Acid Resistance Tests.

The tests for acid resistance under standard conditions gave results as shown in Table 5.

TABLE 5.

	A.	B.	C.	D.	E.	F.
Acid loss.....	0.97 g.	0.65	0.57	0.38	0.24	0.14

These figures express the actual acid loss and are the inverse of acid resistance. They are plotted in Fig. 5. It will be noted

¹ Hovestadt (Jena Glass), page 217.

that, although in "A" nearly 1.0 gram of the pulverized frit was dissolved, in F slightly less than 0.15 g. was dissolved, indicating a very marked gain in acid resistance.

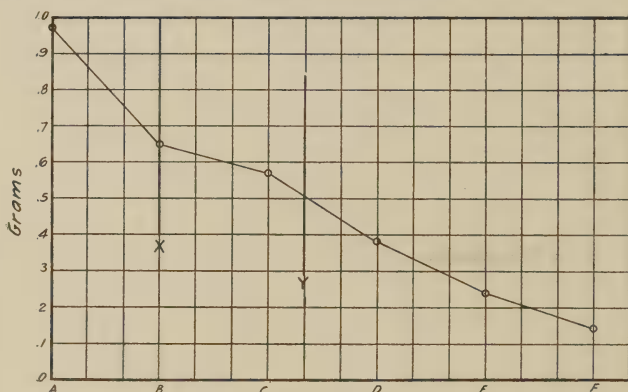


FIG. 5.—Acid loss.

Conclusions.

In general, we may conclude that the chemical composition of a frit at the point of normal pouring may differ quite materially from the composition which would be expected based on theoretical computation. The principal differences in the case at hand are that the SiO_2 content is materially higher, the Al_2O_3 , CaO and K_2O are slightly higher, and the Na_2O and B_2O_3 contents are very much lower than the theoretical composition would indicate. Prior to this point the batch as a whole has passed through a stage approximating the computed composition with the exception of the B_2O_3 content. Further heating produces very marked chemical changes which rapidly increase the SiO_2 content and decrease in like manner the content of Na_2O and the B_2O_3 , when judged from a percentage point of view. Or, assuming the SiO_2 to remain constant after the volatilization of the silicon tetrafluoride, there is a slight volatilization of CaO , Al_2O_3 and K_2O and very marked losses of B_2O_3 and Na_2O .

As a result of these chemical changes, we introduce an objectionable rise in the maturing point of the enamel but a favorable increase in the deformation range. The computed coefficient of

linear expansion drops quite rapidly and at the end of the series it is no doubt sufficiently low to produce shivering. The enamel would have a marked tendency to over-burn and become very brittle when applied to the ware, were the smelting to be continued very far beyond the line "Y." The further smelting would produce a very desirable increase in the acid resistance of the enamel, but it would appear that the resulting objectionable physical properties would make it impossible to realize this increase in chemical resistance.

THE ELYRIA ENAMELED PRODUCTS CO.,
ELYRIA, OHIO.

COMMUNICATED DISCUSSION.

J. B. SHAW: Although the results obtained by the authors of this paper could be more simply expressed by giving the actual formula used, this method of presenting the data is logical and, if carefully considered, reveals practically the same information as could be secured from a study of the results in connection with the formula itself.

Although I do not believe that the use of this method of presenting data should be encouraged—where possible authors should give complete data if their papers are to be of the highest value—I do believe that in case the formulas cannot be given, some method such as the one employed should be devised. Data presented in this manner does not lend itself readily to criticism. However, there are a few points of interest which should be emphasized.

1. The points of the highest acid resistance and the greatest toughness are not coincident in the case of the enamel used. In other words, if great toughness is desired, it is necessary to terminate the fritting just before the point of the highest acid resistance is reached. On the other hand, it is necessary to continue the fritting beyond the point of greatest toughness if high acid resistance is desired. My experience with a number of enamel formulas has confirmed this.

2. The remarkable decrease in B_2O_3 accompanying the increase in SiO_2 appears unusual. To my mind, it is doubtful whether the B_2O_3 volatilizes to the extent indicated under the short heat

treatment. I have found that, in making the chemical analyses of enamels, the B_2O_3 and SiO_2 are separated with difficulty and, unless great care is exercised, some of the B_2O_3 may be included with and reported as SiO_2 .

It would add very materially to our knowledge if a reliable method for the chemical analysis of enamels containing fluorides, boric acid, Sb_2O_3 , SnO_2 , etc., were available.

3. I believe that the influence of the coefficient of expansion as a factor in shivering or crazing is greatly overestimated by enamellers. Fish-scaling is the *bête noir* of the enameling industry—especially of the sheet iron enameling branch. This phenomenon is presumably parallel to that of the shivering of glazes. It is evidenced by the scaling off of small flakes of the enamel and a resultant pitted surface—the steel being exposed in many places. It is supposed to be influenced largely by the coefficient of expansion of the enamel but in a recent set of experiments—involving the use of 120 ground coats of widely different chemical composition and applied to light steel—not one piece showed any fish-scaling when the enamel coating was properly applied and fired. But when improperly ground, applied or burned, or when applied on very heavy steel, fish-scaling was very prevalent. These facts, together with similar experiences in the past, lead me to believe that the mechanical manipulation of the enamel is a far greater factor in controlling fish-scaling than is the chemical composition.

R. R. DANIELSON: The authors of this paper present some interesting facts to the enameler—in that they very forcibly bring out the effects of undersmelting and oversmelting upon the enamel batch. Their conclusion that “variations in the properties of the enamel may be due to the volatilization of certain constituents in the batch” is instructive and may account for the irregularities which occur in the working of enamels—in spite of all the precautions taken in the processes of preparation and application.

Some of the irregularities in the data of this paper may be due to the method of sampling employed. It is quite possible that, in selecting a sample of undersmelted enamel, there might

be certain unfused refractory constituents, such as flint, etc., which would not pulverize as quickly as some of the other substances in the ball mill and which might fuse together to form a soft glass. In screening the sample through a 200-mesh sieve—unless the grinding had been very thorough—the coarser materials might be left on the sieve and consequently be eliminated from the frit. This would be especially true of the undersmelted enamels—since there would not be the homogeneity necessary in properly smelted enamels unless the entire sample were ground very finely and then quartered for the tests. This objection would also apply to the tests for acid resistance as carried out by the authors.

The authors have started a work which should be continued, for it will undoubtedly help to solve some of the problems encountered in enameling.

H. F. STALEY: The losses by volatilization, over and above those ordinarily assumed, are certainly high compared to those encountered in smelting enamels for cast iron. At the point "Y," at which the authors state this enamel would normally be poured, the loss, assuming the SiO_2 content to be constant from A on, is 11.8 per cent. From a series of carefully kept records extending over a period of years, I found that the loss in the smelting of cast iron enamels exceeded the theoretical loss by 1.9 to 3.0 per cent. and that part of this loss could be attributed to mechanical loss in the filling and emptying of the smelter. The difference must be largely due to the difference in composition of the two types of enamels. In the ordinary enamel for cast iron, used in this country, the B_2O_3 content varies from 6 to 12 per cent. The enamel used by the authors evidently contained a larger quantity of B_2O_3 for at "F" (Table 2) the loss by volatilization was 9.5 per cent., a considerable portion remaining in the fritted enamel.

It is noteworthy that the B_2O_3 and the bases were volatilized in approximately equal molecular amounts. This is in accord with results obtained by myself when working with borate glasses.¹ In these glasses, when the molecular ratio of base to B_2O_3 equaled

¹ "The Viscosity of Molten Glasses," Eighth Intern. Congr. Appl. Chem.

or exceeded 1 : 4, the ratio of the most acid pyrogenetic borate, there was no loss of B_2O_3 without loss of the base in the ratio existing in the melt. When the ratio of base to B_2O_3 was lower than 1 : 4, there was a corresponding loss of B_2O_3 .

E. P. POSTE: Mr. Shaw's first point is very well taken and as a general conclusion has been confirmed a number of times. He is slightly in error, however, in his reference to the maximum acid resistance of this enamel. It is shown in Fig. 4 that the acid resistance at F is relatively high but that it has apparently not reached a maximum. In other words, had the smelting been continued a further increase in acid resistance would have resulted.

Our experience in the analysis of the boro-silicates does not confirm that of Mr. Shaw. Our B_2O_3 determinations were made on separate samples, the silica being determined in the usual manner. Fluorine was not found present. We were aware of the possible errors arising in the determination of B_2O_3 and Al_2O_3 and observed the necessary precautions as noted in Mellor's "Treatise on Ceramic Industries," Vol. 1, pages 584 and 589. Had any appreciable error of this nature occurred—the analyses would have totaled materially over 100 per cent. This was not found to be the case.

The remarks relative to the effect of the coefficient of expansion as a factor in fish-scaling are very interesting. Our recent observations have caused us to lose faith in the coefficient of expansion theory for fish-scaling—at least when the coefficient of expansion is alone considered and computed in accordance with the factors given in the Jena researches. We have come to the conclusion that, although this may be one of the factors, there are certainly other more important ones and principally those of elasticity and tenacity as has been so clearly pointed out by Staley.¹

The criticism of Mr. Danielson is very pertinent—in so far as it applies to the method in general. It would perhaps be preferable to grind the entire sample so that it would pass a given mesh sieve rather than to take only that portion which had passed through the sieve. It is doubtful, however, whether the errors

¹ *Trans. Am. Ceram. Soc.*, 14, 523-531 (1912).

resulting from this source could have materially affected the results in this case for it has been our observation that the amount of material retained on a 200-mesh sieve under the particular conditions of grinding was very small. The point is well worth keeping in mind, however.

The figures given by Mr. Staley—relative to the loss on smelting and in excess of the theoretical amount—would indicate a material difference in the types of enamels under consideration. Certain commercial formulas, in use at the present time, show a loss of from 3.0 to 5.0 per cent. in excess of the theoretical amount which we had formerly accounted for in the same way that Mr. Staley accounts for his losses of from 1.9 to 3.0 per cent. We conclude that some of this loss was due to volatilization. The enamel used in our experimental work was considerably softer than the ones concerning which commercial smelting data is available. No doubt the difference in the constitution of the enamels accounts for the apparent differences in the amount of material volatilized.

A COBALT-URANIUM GREEN GLAZE FOR TERRA COTTA.

By HEWITT WILSON, Columbus, Ohio.

We were confronted with the problem of developing a commercial green glaze having a deeper shade than any of the yellow-greens we had produced by the use of chromium stains in glazes fired to cones 6 or 7.

The characteristics and methods of producing green colors in glazes may be outlined as follows:

1. Copper greens are used extensively. At cones 6 or 7, however, the greater part of the copper is volatilized and the resultant shades of green are light and uneven.
2. Chromium and chromium stains when used in most glazes of the Bristol type give greens which appear yellow when compared with deep greens. The chromium can only be used in glazes in which the zinc content is very low. A reduction of the zinc content necessitates either a higher maturing temperature for the glaze or the use of lead compounds or frits. Chromium compounds are unstable in the kiln. In the proximity of even small amounts of chromium, glazes containing zinc oxide fade to brown and glazes containing tin are apt to be streaked with pink.
3. The nickel green colors are variable.
4. Iron compounds, if used alone, are volatilized at cones 6 or 7.
5. Uranium compounds, if used alone, produce variable yellow-green colors.
6. Greens may be produced by the blending of blue and yellow colors.

(a) It is reported that mixtures of iron and cobalt compounds have produced good greens. This has not been our experience—our trials giving browns and brown-greens.

(b) Orton notes the preparation, by roofing-tile manufacturers, of a green sulphate from antimony and cobalt oxides. Various yellow stains—some of which derived their yellow color from

antimony—were blended with cobalt and produced yellow and greenish browns which shaded into blues.

(c) Mixtures of cobalt oxide and titanium compounds are reported to have produced greens.

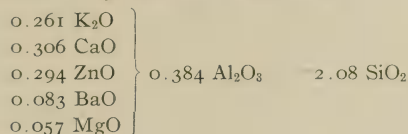
(d) Several investigators¹ have produced greens from mixtures of soluble uranium and cobalt compounds which were added to the glaze as insoluble frits.

In our attempt to develop the shade of green desired the procedure was as follows:

Series A.

Using a dull matt glaze as a base, uranium oxide and a cobalt stain were added to this glaze in varying amounts.

The formula of the glaze was as follows:



This glaze matures at from cones 3 to 7 in a commercial kiln. The blue stain added to the glaze had the following composition:

	Per cent. (Raw).
Cobalt oxide.....	16.0
English ball clay.....	53.0
Zinc oxide.....	31.0
	<hr/>
	100.0

The commercial uranium oxide was supplied by the Carnotite Reduction Co. of Chicago. A rectangular series of 45 members was prepared by the addition of the cobalt stain and uranium oxide to the matt glaze. The corner glazes of the series were as follows:

- Glaze No. 1—Matt glaze + 7.0% uranium oxide + 0.0% blue stain
 Glaze No. 9—Matt glaze + 7.0% uranium oxide + 6.0% blue stain
 Glaze No. 37—Matt glaze + 3.0% uranium oxide + 0.0% blue stain
 Glaze No. 45—Matt glaze + 3.0% uranium oxide + 6.0% blue stain

¹ F. H. Riddle, *Trans. Am. Ceram. Soc.*, **8**, 210 (1906); R. H. Minton, *Ibid.*, **9**, 777 (1907); B. S. Radcliffe, *Ibid.*, **16**, 209 (1914); *La Céramique*, **1907**, No. 225, S. 25; *Tonind. Ztg.*, **1907**, S. 1412.

Each glaze was sprayed upon 3" \times 5" terra cotta tile to which a coating of white underslip had been first applied.

The glazed tiles were placed in a commercial terra cotta muffle kiln and burned to between cones 6 and 7. The burning period was 70 hours and the cooling period 80 hours.

The appearance of the glazes of this series is noted as follows:

Glazes Nos. 1, 10, 19, 28, and 37, containing no cobalt stain, developed the characteristic uranium colors. 3.0 per cent. of

		Uranium Oxide Per cent.				
		7.0	6.0	5.0	4.0	3.0
Cobalt Stain - Per cent.	0	1	10	19	28	37
	0.75	2	11	20	29	38
	1.5	3	12	21	30	39
	2.25	4	13	22	31	40
	3.0	5	14	23	32	41
	3.75	6	15	24	33	42
	4.5	7	16	25	34	43
	5.25	8	17	26	35	44
	6.0	9	18	27	36	45
		Series A Matt Glaze as Base				
		Series B Bright Glaze as Base				

the stain produced a brownish yellow color, changing to green as the uranium content increased. The glaze containing 7.0 per cent. uranium oxide, although green, had a decided yellow cast.

Glazes Nos. 2, 11, 20, 29 and 38 were of deeper green shades and showed the influence of the stain but slightly.

Glazes Nos. 3, 12 and 21 were as green as any of the glazes of the series, but were not uniform when applied on large surfaces.

Glazes Nos. 30 and 39 were mottled by patches of yellow.

Glazes Nos. 4 to 9, 13 to 18, and 22 and 23 were uniformly deep green in color.

Glazes Nos. 24 to 27 developed a distinct blue-green color. The green color faded and the blue became stronger with increasing amounts of the cobalt stain.

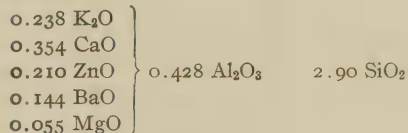
Glaze No. 40 contained the smallest amount of the cobalt stain to show blue tints. When the uranium addition was lowest (3.0 per cent.), the blue shades were obtained with the lowest amounts of blue stain.

The glazes listed above as good deep greens were somewhat defective on account of the occurrence of yellow patches on the surfaces. There was no regularity in the occurrence of this yellow surface mottling. This mottling was very prominent in several of the good green glazes which were applied to full sized pieces of terra cotta. The appearance of the mottling was not very objectionable—in fact was pleasing—although not desired.

Series B.

Using a bright glaze of the following formula as a base, another series was prepared by the addition of the uranium oxide and cobalt stain in the same proportions as in Series A:

Bright Glaze:



This glaze matures at from cones 4 to 7 when fired either in a small or large kiln.

The appearance of the glazes of Series B is noted as follows:

The colors developed were in general the same as those of the Series A glazes, although not as distinct. The green colors tend toward the brown and drab shades. The blue and yellow colors are less pronounced. The addition of uranium oxide alone tends to produce fine dark specks.

The yellow mottling developed by some of the glazes of Series A was not observed in any of the glazes of Series B. The mottling of the glazes of Series A may be explained as follows:

Since the uranium compound is partially soluble, a greater proportion of the yellow material was deposited near the surface of the glaze as the water evaporated in drying. The yellow color of the uranium partly masked the blue color of the insoluble stain and produced the mottled effect. Although the uranium does not come to the surface as a scum, it tends to take possession of the surface and the upper portion of the glaze—leaving a greater proportion of the blue stain next to the underslip. Any particles of blue stain which do appear on the surface are coated with sufficient uranium to appear green. Under the microscope, a cross section of the glaze coating shows that in places where the yellow-green does extend into the mass of the glaze a darker and bluer green results close to the underslip. As the bright glaze used in Series B produced no mottling, we may assume that it had greater solvent power than the matt glaze used in Series A.

Series C.

From the information secured from Series A and B a third series was prepared as follows:

In order to avoid the mottling of the matt glaze, a soluble blue stain was employed—the cobalt being added as soluble cobalt sulphate. Maintaining the uranium content constant at 6.0 per cent., the cobalt sulphate was added to the matt glaze (Series A) in varying amounts. The addition of 3.0 per cent. gave a reliable color, the proportion of uranium to cobalt sulphate in this case being 2 : 1. The matt glazes to which the cobalt sulphate was added were more vitreous than those in which the insoluble cobalt stain was used.

No signs of mottling were in evidence in the glazes of series C and the 3.0 per cent. cobalt sulphate glaze was used in the coating of 200 sq. ft. of terra cotta surface. A green glaze of this description can be burned in proximity to other glazes without danger of discoloring them.

By calcining or fritting the cobalt and uranium to a homo-

geneous mixture and by subsequent fine grinding a similar green can no doubt be obtained.

COMMUNICATED DISCUSSION.

R. L. CLARE: 1. I wish to state that whenever possible we have avoided the use of uranium compounds in terra cotta glazes on account of their excessive cost and we have usually been able to produce the various shades of green desired without the use of these materials.

2. We have used chromium alone in glazes and have found it to be very unstable and unsatisfactory. It, however, in some cases gives a very deep green color, deeper and better in fact than any which we have been able to secure by the use of a stain. It appears that the materials used in a stain with the chromium tend to dilute the green shade. Materials such as iron, cobalt or uranium when used in a stain change the shade to a brown-green, blue-green or a yellow-green.

3. It is very interesting to note that Mr. Wilson has produced a good green by the use of a mixture of uranium oxide and a cobalt stain. It is not clear in my mind whether his resultant green is of the same shade as the typical chromium green. We have produced greens by the use of mixtures of iron and cobalt stains and manganese and cobalt stains, but in each case they have developed yellow-green, blue-green or brown-green colors and in no case were the typical deep grass-greens of the chromium produced.

Mr. Wilson's theory of the cause of the mottling on the glaze surface is very interesting and plausible. We have often noticed scumming on the surfaces of some of our colored glazes and we have attributed it to the solubility of some of the colorants and the consequent concentration of salts on the surfaces of the pieces—due to evaporation. It has already been shown that colors can be produced by painting or spraying certain soluble salts in solution on the surfaces of the unburned terra cotta glazes.

D. F. ALBERY: I wish to note the following in reference to the methods of producing green colors in terra cotta glazes:

1. Copper oxide is satisfactory in glazes fired from approximately cone 04 to cone 2.

2. Chromium alone is too unstable to be recommended for the production of the green colors.

3. Chromium stains when properly compounded, calcined and washed, produce very stable and uniform greens of practically any desired shade. These green shades may be varied from deep blue-greens to brown-greens by the addition of cobalt oxide, iron oxide or burnt umber. The composition of the stain influences its color and shade considerably. For instance, it is possible to vary the shade of a given glaze by substituting plaster of paris for whiting in the stain. The composition of the glaze also has a decided influence on the stability of the color produced by a given stain.

We have made name panels by using a green glaze for the background and a white glaze—containing about 6 per cent. tin oxide—for the raised letters. The white glaze did not show the slightest discoloration even though it was in contact with the green glaze in a line at the base of the letters. It is largely a matter of glaze composition. Our green glazes are not fritted and do not contain zinc or lead.

4. I have never known of an iron compound producing a green color when used alone in a glaze at any temperature.

5. I have produced an unstable yellow-green by the introduction of a high percentage of uranium.

6. I have produced good blue-greens with cobalt-rutile combinations in glazes maturing at from cone 03 to cone 2.

Although good green colors may be obtained by cobalt-uranium combinations, it would appear that the cost of the high percentage of uranium oxide necessary would discourage the extensive use of this method.

R. H. MINTON: Those who have had experience in the manufacture of architectural terra cotta will appreciate the value of a dependable green coloring agent which is not affected by zinc oxide, and which will not affect, or be affected by, other colors. White, greens, browns and tans are widely used in polychrome work and a combination of these colors has always presented difficulties if the green was produced by the use of chromium compounds—the usual practice. Terra cotta white matt glazes

usually contain a high percentage of zinc oxide and, if used next to a chromium green, an unsightly line of tan or brown results at the juncture. For this reason, a green produced from a mixture of uranium and cobalt greatly simplifies the factory operation.

My experience with the use of uranium compounds for yellows and greens has covered its use in both fritted and raw, bright and matt glazes, and has shown that in order to produce a good yellow from uranium in a matt glaze, the zinc oxide should be eliminated as it tends to the development of greens. I have found that in order to produce uniform uranium colors, either yellow, orange or green in a matt glaze, it is of great advantage to use a small amount of rutile. The rutile appears to "set" the color and prevent the irregularity of color so often produced by uranium. An excellent green may be produced by the use of cobalt and rutile with the addition of a small amount of oxide of iron, although the color is not quite so bright as that secured with the presence of some uranium.

The mottling of the color in the matt glaze is undoubtedly due to the failure of the glaze to dissolve the uranium and the consequent crystallization or segregation, upon cooling. This difficulty is almost always encountered in producing uranium yellow matt glazes, where reducing conditions may occur, the result being a mottled green-yellow. The addition of rutile will entirely overcome this defect and the color will be improved if the content of zinc oxide is kept very low. A high zinc content and reducing atmosphere in the kiln are favorable for the production of greens. The use of the soluble form of the cobalt, rather than the difficultly soluble stain, as stated by Mr. Wilson, probably caused the formation of the green color by solution of the cobalt and uranium instead of by suspension.

HEWITT WILSON: The uranium-cobalt greens developed in the above study are not of the same shade as the typical chromium greens. The color is a deeper green than that afforded by the majority of the chromium greens burned in terra cotta muffle kilns to cone 6. While it is true that the cobalt-uranium greens do not match the characteristic chromium greens, it is likewise

true that it would be difficult to match some truly acceptable uranium-cobalt green shades with chromium combinations.

There is no question as to the practicability of producing green colors from cobalt and uranium mixtures. They have been produced in regular terra cotta work in a quantity sufficient to insure the uniformity required.

The disadvantages of the high cost of uranium is not so great when the comparatively small amount of green glazed terra cotta produced is considered. We do not know of any single component for colored glazes which has caused more terra cotta trouble than chromium.

The advantages of the above uranium oxide-cobalt sulphate green are as follows:

1. Ease of preparation. No calcining, washing or extra grinding necessary.
2. So far as noted, there was almost no discoloration of adjoining glazes—regardless of their composition.
3. A greater range of glaze composition in which green colors can be produced. It can be used in zinc and tin glazes.

Although it is not claimed that uranium-cobalt greens will replace the chromium greens, they have a place in terra cotta work in which uranium shades are desired and the complexities of chromium troubles are to be avoided.

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ALABASTER GLASS: HISTORY AND COMPOSITION.

BY ALEXANDER SILVERMAN, Pittsburgh, Pa.

Alabaster is a term usually applied to semi-opaque glasses which transmit the light from a source, diffusing it, but not materially altering its color. The name was probably applied because of the close resemblance which these glasses bear to natural alabaster. The French use the term "Albatre" or "Pate de Riz" (rice paste). Opal glasses are also semi-opaque but the light transmitted acquires an opal or fiery color.

During researches by the writer on the production of alabaster and opal effects considerable historical material has been gathered and is presented here for ceramists who may be interested.

In the museum exhibits one frequently encounters collections of Chinese snuff bottles which are made of alabaster glass. Some of these,¹ coming from the Ch'ien Lung dynasty (1736-1795), are almost 200 years old. According to one authority, alabaster glass was made in Venice and Murano at about 1600. Some early Egyptian glasses show slight alabaster effects which are probably due to imperfect melting or to devitrification during the ages in which they lay buried.

"Manuel Complet de Verrier," by M. Julia de Fontenelle, published in Paris in 1829, mentions alabaster glass on page 30.

H. Leng² speaks of the use of lead sulphate in the manufacture of opal glass. The writer's experience, certain details of which will be given later, points to alabaster formation in the presence of sulphates, so it is possible that Leng's opal was alabaster.

Deming Jarvis³ gives the following formula for alabaster glass: "500 lbs. batch (probably crystal glass), 30 lbs. phosphate of soda, 10 lbs. allumine (calcined alum), 3 lbs. calcined magnesium." On page 116, Jarvis states that alum loses 60 per cent. on cal-

¹ Carnegie Museum, Pittsburgh, Pa.

² "Handbuch der Glasfabrikation," 1854.

³ "Reminiscences of Glass Making," New York, 1865, p. 106.

cining. Assuming its conversion to Al_2O_3 and K_2SO_4 , it should lose 70.8 per cent., and it is therefore probable that the material was either partly decomposed potash alum or some other substance called alum in that day.

Hoch¹ mentions alabaster as one of the oldest known glasses and states that melasse (beet sugar potash bearing sulphates and chlorides) was employed.

Raimund Gerner² mentions the use of salt in the preparation of cloudy glass and gives the following formulas:

1.		2.	
	Parts.		Parts.
Sand.....	100.0	Sand.....	100.0
Slaked lime.....	2.0	Slaked lime.....	13.0
Bone ash.....	5.5	Tin oxide.....	1.0
Potash.....	44.0	Potash.....	38.0
Salt.....	5.5	Salt.....	1.5
Arsenious oxide.....	0.7	Arsenious oxide.....	0.25
Cullet.....	50.0	Borax.....	1.0

It is unlikely that the alabaster effect was produced by the salt alone. The bone ash probably functioned in batch 1 and the tin oxide in batch 2, and the arsenious oxide in both.

Before the extensive working of the Stassfurt mines in Germany, much of the potash was derived from plant ashes and large quantities were imported from Russia. This material contained considerable quantities of sulphates and chlorides which were partly conducive to the production of the alabaster effect.

In the second edition of Gerner's book, Leipzig, 1897, page 211, is given the following batch:

	Parts.		Parts.
Sand.....	50	Cryolite.....	7
Soda.....	8	Litharge.....	2
Alumina (Alaunerde).....	4	Lime.....	3
		Saltpetre.....	2

On page 34 of the same publication he states that "potash, until very recently, was prepared from wood and plant ashes. Beech ashes (Buchenholzasche) contain K_2CO_3 15 per cent.,

¹ *Dingler's polytech J.*, 224, 623 (1877).

² "Die Glasfabrikation," Vienna, 1880, p. 267.

Na_2CO_3 3 per cent., K_2SO_4 2 per cent., and the remainder water-insoluble matter." On page 35 he states that "Refined beet potash contains K_2CO_3 92 per cent., Na_2CO_3 5 per cent., KCl 3 per cent., also K_2SO_4 ." On page 36 he gives the following analyses of potashes:

	K_2CO_3 .	Na_2CO_3 .	K_2SO_4 .	KCl .
American potash.....	71	8	16	3
Illyrian potash.....	89	0	1	9
Russian potash.....	69	3	14	2
Wool Sweat (Suint).....	72	4	6	6
Refined Beet Ashes (Melasse)....	90	2	3	3
Stassfurt.....	97	0	1	1

On page 59 he dwells upon the use of spars and alumina and on page 212 states that "alumina may be substituted for the cryolite, feldspars, etc."

Gessner¹ refers to the use of alumina in quantities of from 7 to 20 per cent.

Furnival² states that American pearlash contains about 7 per cent. K_2SO_4 .

Hans Schnurpfeil³ also calls attention to the presence of sulphates and chlorides in potash.

Fontenelle and Malepeyre⁴ state that equal parts of chalk and Al_2O_3 when melted together yield a glass resembling pearls, and give a formula for the preparation of a white, translucent glass, as follows: Sand 100, chalk 32, Al_2O_3 68. In vol. II, p. 242, they discuss the manufacture of alabaster glass in Bohemia.

Paul Randau⁵ gives the following alabaster batch containing sulphates:

100 parts	Feldspar.....	35 to 71 parts
	Fluorspar.....	17 to 50 "
	Barytes.....	12 to 40 "
melted with	Soda.....	15 to 50 "
	or Potash.....	20 to 65 "
	and Sand.....	70 to 120 "

¹ *Glassmakers Handbook*, Pittsburgh, 1891, p. 148.

² "Researches on Leadless Glazes," 1898, p. 54.

³ "Schmelzung der Glaser," 1906, p. 11.

⁴ "Manuel du Verrier," Paris, 1, 59 (1900).

⁵ "Die Farbigen, Bunten and Verzierten Glaser," Vienna, 1905, p. 106.

These proportions are also given in a patent¹ granted to J. Kemper.

An article by Richard Zsigmondy² on "Cryolite and its Substitutes," mentions the use of china clay and sodium fluoride in alabaster batches, stating that the best results are obtained by adding a quantity of china clay equivalent to the sodium fluoride in the cryolite.

The following formulas³ are suggested for the use of alumina and sodium fluoride:

	Parts.	Parts.
Sand.....	100	100
Sodium fluoride.....	10	6
Alumina (Alaunerde).....	14	10
Fluorspar.....	0	10
Feldspar.....	0	8

The use of sodium fluoride in alabaster glass is covered in a patent⁴ issued to Adolf Tedesco, who gives the following formula:

	Parts.
Sand.....	156
Sodium fluoride.....	33—(containing 10 per cent. sodium carbonate)
China clay.....	15
Chalk.....	10
Soda.....	5

In this patent the inventor claims the use of sodium fluoride only, so that the use of alumina in alabaster batches must have been known to glass makers.

Weinreb⁵ mentions the use of a mixture of SiO_2 100 parts, Na_2F_2 20 parts, K_2CO_3 8 parts, Na_2CO_3 7 parts, CaCO_3 8 parts, and $\text{Al}_2(\text{OH})_6$ 6 parts, which, he states, yielded a beautiful, white glass.

In the *Journal of the Society of Chemical Industry*⁶ is noted a statement that "Since, however, fluorine (from cryolite) attacks the glass-pots and thus leads to contamination of the glass,

¹ D. R. P. 4551, July, 1878, *Dingler's polytech. J.*, **233**, 269 (1879).

² *Ibid.*, **271**, 40 (1889).

³ *Sprechsaal*, **30**, 556 (1897).

⁴ D. R. P., 31,112, November, 1883.

⁵ *Dingler's polytech. J.*, **256**, 365 (1885).

⁶ *J. Soc. Chem. Ind.*, **18**, 916 (1899).

feldspar or alumina is sometimes added, the composition of the mass being modified as follows: Sand 50 parts, potash 4 or 5 parts, soda ash 5 or 6 parts, cryolite 7 parts, feldspar or alumina 5 parts, lime 5 parts, and nitre 3 parts. A cheap substitute for cryolite is fluorspar which, however, has to be neutralized by alumina in order to prevent corrosion of the pots, etc. A typical mass is prepared from a mixture of sand 50 parts, soda ash 8 to 10 parts, potash 3 to 4 parts, fluorspar 10 parts, alumina 5 to 10 parts, nitre 2 to 3 parts, zinc white 2 to 3 parts, feldspar 0 to 10 parts, etc. A mixture of sodium fluoride and alumina is also cheaper than cryolite, etc. The mass is compounded from a mixture of sand 50 parts, potash 6 parts, soda ash 6 parts, sodium fluoride 4 to 6 parts, alumina 5 to 8 parts, feldspar 6 parts, nitre 1 part, minimum 3 parts, or zinc white 2 parts, and lime 0 to 3 parts."

The references cited in the preceding paragraphs show clearly that the use of mixtures of alumina, sulphates and chlorides with other raw materials is not original with American chemists and manufacturers although they have produced some of the finest alabaster glasses of superior quality and commercial value. No explanation of the cause of the alabaster effects is offered by the early writers except that of devitrification. The author believes that sulphates and chlorides serve as ionized electrolytes in the hot liquid, precipitating various colloidal suspensions which would otherwise cause opalescence.¹

In the writer's researches on alabaster glass a number of interesting facts have been developed. Fluorides with alumina or aluminium bearing substances produce opalescence until sufficient quantities of sulphates or chlorides are introduced when the opacifying materials gather in larger particles and white light is transmitted. The bivalent ion of the sulphates produces more intense whiteness than the monovalent chloride. This is in keeping with the behavior of electrolytes towards aqueous colloidal suspensions.

The presence of barium² compounds enhances the white color—

¹ A. Silverman, "Similarity of Vitreous and Aqueous Solutions," *J. Ind. Eng. Chem.*, **9**, 33 (1917).

² A. Silverman, "The Use of Barium Compounds in Glass," *J. Soc. Chem. Ind.*, **34**, 399 (1915).

probably through the formation of barium fluosilicate. Cryolite produces increasing whiteness up to a certain concentration. The color then gradually loses intensity with the introduction of larger quantities and finally disappears. This effect resembles the solution of precipitates in aqueous solutions in the presence of an excess of the precipitant.

Alumina and the chlorides were employed in the writer's researches prior to 1904 and sulphates were introduced in 1912. As the result of these researches a commercially successful alabaster glass¹ of American manufacture was placed on the market. The limited solubility of the chlorides and sulphates in the silicates led to a considerable reduction of the quantities introduced into the batch, with an accompanying increase in the life of the pots which are attacked by fused chlorides and sulphates.

When the alumina was replaced by its equivalent of feldspar, a beautiful, speckless glass of much higher than normal viscosity resulted. Magnesium silicate also produced the alabaster effect. The following formulas for American alabaster glasses are contained in patents:²

	Parts.		Parts.
Sand.....	100	Sand.....	345.8
Lead oxide.....	15 ⁵ / ₈	Litharge.....	56.8
Soda.....	21 ⁷ / ₈	Soda ash.....	86.4
Niter.....	5 ¹ / ₂	Cryolite.....	20.0
Salt.....	5 ¹ / ₂	Aluminium oxide...	60.0
Borax.....	1 ¹ / ₄ to 2 ¹ / ₂	Niter.....	32.0
Aluminium hydroxide..	18.12	Borax.....	8.0
Fluorspar.....	6	Plaster of paris....	5.0
		Parts.	
Sand.....	100		
Soda ash.....	49		
Red lead.....	56		
Feldspar.....	120		
Sodium fluoride.....	7 ¹ / ₂		
Strontium sulphate.....	1 ³ / ₄		
Sodium chloride.....	5		
Alumina.....	22 ¹ / ₂		
Niter.....	5		
Antimonious oxide.....	1 ¹ / ₂		

¹ A. Silverman, "The Chemist and the Glass Manufacturer," *Trans. Am. Ceram. Soc.*, 12, 187 (1910).

² U. S. Patents 1,097,600-1,143,788 and 1,245,487.

Although the most desirable alabaster glasses are produced by aluminium-bearing substances with fluorides and chlorides or sulphates, this article would not approximate completeness without mention of other types given in the literature. Calcium phosphate, magnesium silicate, stannic oxide, arsenious oxide, zirconium oxide¹ and titanium oxide² are also employed. Analyses of some alumina-bearing alabaster glasses have revealed the presence of considerable quantities of zirconia, presumably introduced as an impurity in the alumina.

Alabaster effects may also be obtained in high silica glasses through devitrification. Raimund Gerner³ suggests the following batches:

	1.	2.	3.	4.
Sand.....	200	200	250	100 parts
Pearlash.....	80	70	100	42 "
Bone ash.....	12	10	15	.. "
Magnesium silicate.....	9	3	14	8 "
Arsenious oxide.....	1	1 "
Saltpetre.....	..	10	15	5 "

Wilhelm Mertens suggests:⁴

	1.	2.	3.
Sand.....	75	75	100 parts
Pearlash.....	28	30	38 "
Bone ash.....	7	7	.. "
Saltpetre.....	6	8	4 "
Magnesium silicate.....	..	10	10 "
Red lead.....	12 "
Arsenious oxide.....	1	0.5	.. "

Randau⁵ gives this batch: Sand 100 parts, calcium carbonate 40 parts, talc 5 parts and borax 5 parts.

Rudolf Hohlbaum⁶ suggests:

¹ D. R. P., 189,134.

² D. R. P., 18,708.

³ "Die Glasfabrikation," p. 206.

⁴ "Die Fabrikation und Raffinierung des Glases," p. 214.

⁵ "Die Farbigen, Bunten und Verzierten Glaser," 1905, p. 112.

⁶ "Herstellung, Bearbeitung und Verzierung des Feineren Hohlglases," 1910, p. 135.

	1.		2.		3.
Sand.....	100 kg.		100 kg.		100 kg.
Pearlash (65 %).....	41 kg.	(80 to 85 %)	45 kg.	(60 to 65 %)	40 kg.
Calcite.....	...		17 kg.		...
Bone ash.....	...		11 kg.	Guano	7 kg.
Magnesium silicate....	10 kg.		...		2 kg.
Saltpetre.....		3 kg.
Manganese dioxide....	200 g.		200 g.		200 g.
				4.	
Sand.....				100 parts	
Pearl ash (60 to 65 %).....				39 "	
Red lead.....				30 "	
Boric acid.....				7 "	
Saltpetre.....				4 "	
Bone ash.....				2 "	
Stannic oxide.....				2 "	

Additional formulas are mentioned in other books and in journals. Most of these batches fail to work in American factories. They are usually intended for low temperature slow melting furnaces. In some foreign factories the glass is ladled into water and then remelted.



It may now prove of interest to consider the break of continuity in the history of alabaster glass caused by the introduction of opal glass. The earlier white glasses were chiefly alabaster, due, as has already been intimated, to the effect of chlorides and sul-

phates, present as impurities in the various types of potash, and causing the precipitation of the colloids in the glass. When the purer refined pearl ash, prepared from Stassfurt salts and sugar beet waste, became available the absence of powerful electrolytes, or the presence of only very small quantities of electrolytes, prevented precipitation and the smoother opal glasses came into general use. During the latter decades of the nineteenth century opal glass displaced alabaster to a great extent. When American manufacturers succeeded in preparing it on a commercial scale in the early part of the present century they felt that they had made a discovery. What they really had done was to introduce the chloride or sulphate, missing in the pure pearl ash, and so necessary for precipitation. In other words, they obtained through the application of scientific principles a result which impurities in their raw materials had accidentally given to the foreign manufacturers.

The writer conducted an extensive correspondence with glass makers in England, France, Belgium, Italy, Germany and Austria during 1913 in order to secure definite historical data in reference to alabaster glass. The diversity of opinion which follows shows how difficult it is to settle such questions. The date indicates the year in which the manufacture of alabaster glass began according to the informant whose name is given. Where the date is marked (S) a specimen was received which is in the writer's collection. (M) indicates that the informant manufactured alabaster glass. A photograph of some of these specimens is shown on the preceding page.

MANUFACTURERS OF ALABASTER GLASS.

- | | |
|------|---|
| 1600 | The Venice & Murano Co., Venice, Italy. |
| 1700 | Josef Janke & Co., Haida, Austria. (Manufactured by Chinese and Japanese.) |
| 1810 | Josef Knizek, Ullersdorf, Austria. |
| 1810 | E. Michel & Co., Teichstadt, Austria. |
| 1810 | Josef Rindskopf's Soehne, Teplitz-Schoenau, Austria. |
| 1810 | J. Schreiber & Neffen, Wien, Austria. |
| 1820 | Josef Janke & Co., Teichstadt, Austria. (1820 Haida, Bohemia. After 1840 in nearly all Bohemian huts. Made with Russian potash instead of ordinary potash. Many old specimens in Janke museum.) |

- 1830 Josef Rindkopf's Soehne, Dux, Austria. (Made by father in Tischen, Austria, 1860.)
- 1840 M Wilhelm Kralik, Johann Mayer Factory, Winterberg, Austria.
- S 1840 Compagnie des Cristallerie de Baccarat, Paris, France.
- 1840 M Meyer & Neffen, Winterberg, Austria.
- 1850 M Brueder Gerhart, Mulan and Podiebrad, Austria.
- S 1850 Jilck & Vetter, Steinschoenau, Austria. Colored by bone ash, talc and magnesium silicate.
- 1850 M Carl Goldberg, Haida, Austria. Has piece manufactured by father in 1850.
- 1850 M Arthur Rudd & Co., Lancashire, England. (Also made at Birmingham, Stourbridge and London.)
- 1850 M Molineux Webb & Co., Ltd., Manchester, England. (Trade name "Carnelian.")
- S 1860 M E. Michel & Co., Teichstatt, Austria.
- S 1863 Herman Heye, Hamburg, Germany. (Bowl in illustration.)
- S 1864 M Bartles, Tate & Co., Manchester, England. (Trade mark "Cornelian.")
- S 1860 M Raimund Knospel and Soehne, Hillemuehl, Austria.
- 1860 M E. St. Clair (Crystallerie de Baccarat), London, England. (Trade Mark "Agate.")
- 1870 M J. Schreiber and Neffen, Gr. Ullersdorf, Austria.
- S 1870 M Tietze and Seidensticker, Penzig, Germany.
- 1870 M Constantin Kopp, Klein-Anjezd, Austria.
- 1880 M August Walter Soehne, Moritzdorf, Germany. (Vases and illuminating ware.)
- 1880 M Josef Palme, Post Kitlitz, Austria.
- 1880 M Glashuetten-Werke Carlsfeld, Carlsfeld, Germany.
- S 1884 M Anton Rueckel & Sons, Nischberg, Austria.
- S 1888 M Joseph Knizek, Ullersdorf, Austria. (Small vase in illustration made by father. Batch: sand 150, potash 65, magnesium silicate 7, saltpetre 6, bone ash 8.)
- 1890 M Wilhelm Kralik Sohn, Eleonarehhain, Austria.
- S 1892 M Val Saint Lambert Glassworks, Belgium. (Lamp fount in illustration.)
- 1898 M Glasindustrie Schreiber Aktiengesellschaft, Berlin, Germany.

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(See *Sprechsaal*, *Keram Rundschau*, *Glas-Industrie* and *Diamant*, complete sets of which were not available in Pittsburgh when this list was prepared.)

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THE ZWERMANN TUNNEL KILN AND ITS OPERATION.

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It would appear that the following points are essential in the construction and operation of a successful tunnel kiln:

First, as the tunnel kiln, on account of its fuel and labor-saving qualities, is intended to replace the periodic kiln, it would appear that it must be so constructed and operated as to enable one to produce the same conditions as in a periodic kiln.

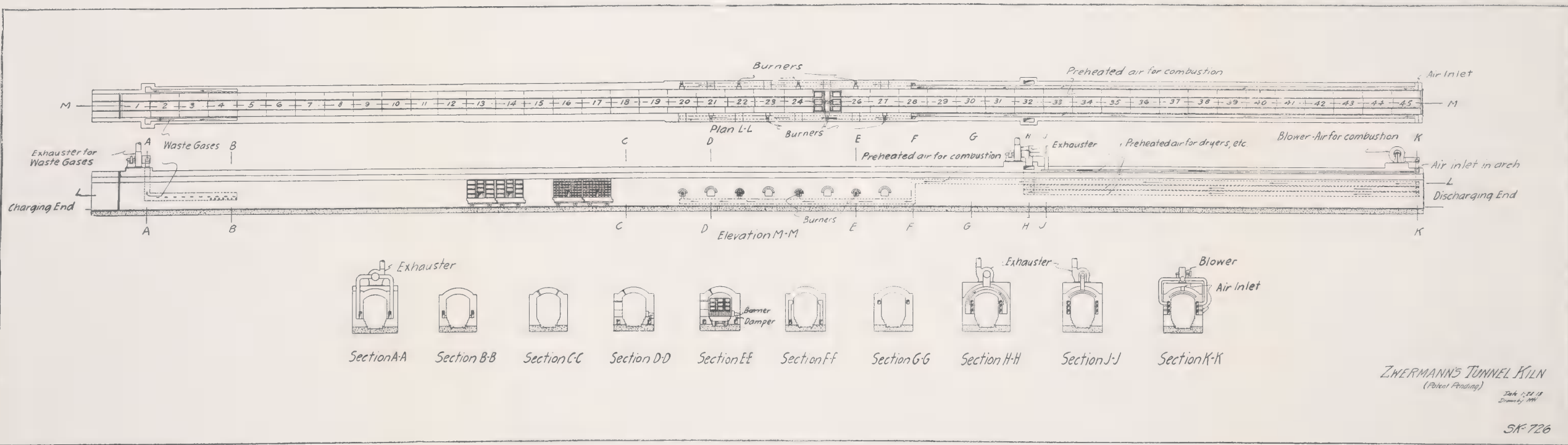
Second, the success of a tunnel kiln depends more upon having it under good control than upon any other factor.

Third, as the first cost of a tunnel kiln is considerably higher than that of a number of periodic kilns of equal capacity, it should be so constructed as to have a comparatively wide tunnel. A tunnel kiln twelve feet wide costs comparatively little more than a tunnel kiln four feet wide, and has about three times the capacity—the heat loss through radiation being proportionately less.

Fourth, the design of the kiln should be as simple as possible so as to require the minimum of repairs. It must be so constructed as to reduce to a minimum the heat losses through radiation and so as to utilize the heat from the cooling zone for drying or heating purposes.

The Zwermann oil-fired kiln, illustrated in Fig. 1, is being operated at Kalamazoo. This kiln is about 352 feet long, including the vestibule, the tunnel being 6' 4" wide and 6' 6" high from the top of the trucks to the arch. It will hold 46 trucks, including the one in the vestibule, each truck being 7' 7½" long. There are nineteen trucks in the preheating zone up to the first burner, eight trucks in the firing zone and eighteen trucks in the cooling zone.

The entrance to the kiln is through a vestibule provided with two tightly fitting rolling doors. A rolling door was originally provided at the outlet end of the kiln but this has been found unnecessary. A hydraulic pusher is installed at the entrance to



the kiln, the pusher rod passing through an opening in the vestibule door, the entire train being advanced one truck length at a time. About three minutes are required to introduce and remove one truck. The loaded trucks are introduced at two-hour intervals, 92 hours being required to pass a truck through the kiln.

The kiln gases are drawn off by means of an exhaust fan near the entrance end. The waste gas outlets are at the fourth truck from the vestibule, on a level with the tops of the trucks, and lead through a flue in the sides of the kiln, extending as far as truck No. 1 and then out through the exhaust. Mechanical draft was preferred as it permits of closer control than stack draft. A second exhaust, located about midway in the length of the kiln, draws cold air through the hollow arch and side walls of the cooling zone of the kiln and passes it through the ware. This pre-heated air is utilized in the drying and pre-heating of the ware. The ware is indirectly cooled by this air, which does not pass through the tunnel or come into contact with the ware. The heat from the cooling ware in both kilns is sufficient to heat the factory and dryers during very severe weather.

The pressure blower, which delivers the air for combustion to the burners, is located on the outlet end of the kiln. This air is passed through recuperators built in the side walls of the cooling zone.

The trucks are of substantial steel construction with cast iron wheels and have a plate on either side which runs in a sand seal. Each truck is covered with a layer of insulating material, on top of which is placed a layer of fire brick tiles. The ware is stacked around and above a combustion chamber which is built on the center of each truck. This combustion chamber is at right angles to the tunnel.

The kiln walls are constructed from a layer of 9" fire brick, 8½" of common brick and a variable thickness of kieselguhr. The arch is built of 9" fire brick and is also insulated with kieselguhr. The insulation of a tunnel kiln is very necessary in order to reduce the heat losses through radiation. Temperature readings, taken at a point at which the internal temperature of

the kiln was 1430° F., gave 102° F. at the surface of the outer wall and 120° F. at the surface of the top of the arch. At another point, at which the internal temperature was 2300° F., the outside surface temperature was 135° F. and the surface temperature of the top of the arch was 142° F.

The ten oil burners used are located on both sides of the kiln. At the two last trucks in the firing zone the burners are opposite each other, the balance being located alternately on either side of the kiln. Eight trucks, in all, are opposite the burners. The location of the trucks in the kiln is so arranged that when at rest the center of each combustion chamber on a truck is opposite the center of a burner.

The oil is delivered to the burners under pressure and is atomized with compressed air. The balance of the air for combustion is supplied, pre-heated, by the pressure blower as already described. All of the air for combustion is blown through the burner blocks and excellent combustion is continually maintained in the combustion chamber. With the arrangement of the burners and air supply described, the kiln may be operated either with a reducing or oxidizing fire by a slight change of the dampers controlling the air supply. This is very necessary in the burning of certain classes of products. In a periodic kiln the atmosphere is somewhat reducing after every coaling and oxidizing after the fires have burned down. The same condition may be created in the Zwermann kiln with little or no difficulty.

The combustion chamber, being built on the truck proper, the making of repairs is simplified and the heat is delivered directly to the center and at the bottom of the material being burned. This, and the fact that the kiln is under excellent control, assures an even distribution of heat and a very uniform firing of the ware. Furthermore, the location of the combustion chambers on the trucks and transversely to the tunnel permits the building of a much wider kiln.

For wares burned in saggers, a combustion chamber on the top of each truck is required in order to permit of the ware being stacked. If bricks are being burned no special combustion cham-

ber structure is necessary—the brick being set so as to form their own combustion chamber.

The burners may be regulated at will and the desired temperature maintained at each one. Eight thermocouples are inserted through the arch in the heating zone of the kiln at Kalamazoo. These are connected to a recording galvanometer. By providing the necessary sight holes in the burning zone the burning may be regulated by means of cones—although better control is had by the use of pyrometers. The desired temperature is maintained for days and weeks without the pyrometer charts showing large variations. The temperature of the ware when it reaches the first burner is about 1000° F. After the temperature desired at each burner has been determined it can be maintained without great variation.

The waste gases leave the kiln at a temperature of about 300° F. Obviously, the percentage of excess air introduced into the kiln is controlled by the regulation of the exhaust.

The quantity of the ware loaded on the cars has been found to be an unimportant factor in the operation of this kiln. When the kiln was first started, there was not enough ware on hand and some empty trucks were passed through. Those following were loaded only to one-half of the height of the tunnel. In every instance, however, the ware was well burned, no over-burned or under-burned pieces being noticed. This was probably due to the location of the combustion chambers at the top of the trucks as well as to the method of firing and regulating the kiln.

We have determined that if the pressure blower, supplying the outside air and also the preheated air from the cooling zone for combustion, was cut out, a large percentage of defective ware and uneven firing resulted. A difference of as high as two cones, between the top and bottom of the truck, was noticed. The highest temperature was at the bottom, although when the kiln was operated under proper control the greatest difference in temperature found between the top and bottom of a truck load was about one-half cone—the ware being burned to cone 9.

The first kiln erected at Kalamazoo is 352 feet long; the second kiln is 285 feet long. Although a longer kiln permits the for-

ward movement of the trucks at shorter intervals, the length of a kiln should obviously be dependent upon the capacity desired and the material to be burned.

Summary.

The experience gained during the period in which the Kalamazoo kiln has been operated demonstrates that, in order to produce marketable ware of any kind and particularly sanitary porcelain, an absolute and convenient control of the kiln is necessary in order that the human factor may be eliminated as far as possible.

It is our conviction that the Zwermann kiln may be used in place of the periodic kilns in the firing of many kinds of ceramic wares. The water-smoking and pre-heating zones are under better and more even control than in a periodic kiln. The cooling of the ware is done just as efficiently as in a periodic kiln. By the use of the tunnel kiln we have made a considerable saving in fuel over that required in the firing of the periodic kilns. A considerable saving in labor has also been noted. A skilled fireman is not required. As the trucks are loaded and unloaded in the open, this work is also lighter and easier and does not require the services of skilled kiln setters.

THE PROPERTIES OF SOME OHIO AND PENNSYLVANIA STONEWARE CLAYS.¹

By H. G. SCHURECHT, Columbus, Ohio.

Introduction.

The resistance of vitrified clay to chemical action, together with its impenetrability to liquids, has made chemical stoneware an important product in the chemical industries. Stoneware distilling kettles, receivers, filters, condensing worms, centrifugal pumps, acid-proof pipe fittings, tower packing, acid-proof tanks, photographic tanks, and troughs and tubes for electrical purposes are used in these industries. Stoneware equipment is also used in the various food industries, including the sugar industry. Owing to the increased production of explosives during the war, there has been a marked increase in the demand for chemical stoneware and for stoneware clays. The wider use of chemical stoneware is only limited by its comparative brittleness and its sensitiveness to sudden temperature changes.

Composition and Properties of Chemical Stoneware.

The clays or bodies used in the manufacture of chemical stoneware should have good bonding power, a small drying and burning shrinkage, and a somewhat wide vitrification range. Crushed stoneware is sometimes added to reduce the shrinkage. Feldspar or a mixture of feldspar and a small percentage of calcium carbonate is sometimes added as a flux. Since the color of chemical stoneware is not an important consideration, cheaper fluxes, such as phonolite, trachyte, porphyry, and retinite, have been used in Europe² in place of feldspar. The chemical analysis of a variety of phonolite is as follows:

¹ By permission of the Director, Bureau of Mines.

² Kerl, B., Cramer, E., and Hecht, H., *Handbuch der gesammten Thonwaren industrie*, Friedrich Vieweg und Sohn, Braunschweig, 1907, p. 1320.

SiO ₂	50.09
Al ₂ O ₃	23.96
Fe ₂ O ₃	2.30
CaO.....	1.22
CaSO ₄	1.41
MgO.....	0.28
K ₂ O.....	9.28
Na ₂ O.....	8.05
H ₃ PO ₄	0.05
CO ₂	0.22
H ₂ O.....	3.27

 100.13

These minerals are found in this country in Texas, South Dakota, Wyoming, Missouri, Minnesota, Utah, Arizona, and Colorado.¹ Albany slip is also sometimes used as a flux in chemical stoneware.

There are many different uses for chemical stoneware and hence the body must be varied to meet the different requirements. Corundum² is sometimes added to the body in case unusual resistance to temperature changes is necessary. In case the ware must be unusually resistant to chemical action—a high degree of vitrification is desirable. For certain purposes, the ware should be very resistant to shocks and strains and therefore the body should be unusually tough and strong when burned. The physical properties of the ware are as important as the chemical properties.

A salt or slip glaze is commonly used in the manufacture, although a glaze corresponding to the formula of cone 1 is sometimes employed for ware which is burned to cone 4. Carborundum,³ because of its resistance to chemical action, is sometimes applied as a coating on chemical stoneware—water glass or boric acid being used as a binder.

¹ Clarke, E. W., "Analyses of Rocks," *U. S. Geol. Surv. Bull.*, **591**, 376 (914).

² D. R. P. Nr. 158,336.

³ Kerl, B., Cramer, E., and Hecht, H., *Op. cit.*, p. 961.

The Occurrence of the Clays Investigated.¹**Tionesta Clay, Ellis, Ohio.**

A sample of Tionesta clay, from the drift mine of Joseph Moody, located one mile south of Ellis, Muskingum County, is designated as "A" in the text. This clay is shipped to the potteries at Zanesville and Cambridge, Ohio, and is used in the manufacture of art ware, mosaic tile, and cooking ware. The sample was taken from a stock pile of the clay. The vertical section of the mine is as follows:

	Ft.	In.
Shale.....	15	0
Limestone, Putnam Hill.....	4	9
Clay and shale.....	12	0
Sample "A" Clay, light, plastic, Tionesta....	4	10

Lower Kittanning Clay, Roseville, Ohio.

The sample was taken from an open cut mine of the Hydraulic Press Brick Co., at Roseville, Muskingum County, and is designated as "B" in the text. This bed has a sufficient surface covering so as to be unaffected by weathering. A vertical section is as follows:

	Ft.	In.	
Shale.....	12	0	
Shale, dark.....	0	2	
Coal, rough.....	0	6	} Middle Kittanning
Shale.....	0	3	
Coal.....	1	7	
Clay.....	0	1/2	
Coal.....	1	9	
Clay, siliceous.....	1	2	
Sandstone, irregular bedded.....	3	2	
Shale, gray.....	7	0	
Sandstone, shaly.....	3	6	
Shale, gray.....	6	4	
Coal, shaly.....	0	1	
Clay, plastic, dark gray.....	5	0	} Oak Hill
Clay, plastic, with large nodules of ferruginous limestone.....	2	0	
Clay, plastic light.....	1	0	
Clay, flint, light gray.....	3	0	
Coal, smutty, lower Kittanning....	0	1	
Sample "B" Clay, plastic, light to dark gray..	6	8	

¹ The Ohio clays were sampled by Mr. Wilbur Stout of the Ohio Geol. Survey.

Lower Mercer Clay, White Cottage, Ohio.

The sample of Mercer Clay, designated "C," was taken at the open cut mine of W. F. Gerhart, located about one mile west of White Cottage, Muskingum County. This clay is used extensively by the Muskingum Pottery Co., White Cottage, and by the A. E. Hull Pottery Co., Crooksville. Although the bed is under shallow covering, the clay is but little weathered. A vertical section is as follows:

	Ft.	In.		
Limestone, Lower Mercer.....	1	1		
Shale.....	0	3		
Coal, bony.....	0	2	} Middle Mercer	
Coal, good.....	0	3		
Clay, light, siliceous.....	2	10		
Coal, shaly.....	0	3		
Clay, siliceous, light, lower part ferruginous.....	5	0		
Sample "C"	Clay, dark, flinty, siliceous.....	0	11	} Lower Mercer
	Clay, plastic, light gray.....	1	8	
	Clay, light, siliceous.....	1	9	
	Clay, dark, somewhat shaly.....	1	8	
	Clay, light, siliceous, hard.....	3	1	
	Clay, light, plastic.....	1	2	

Mogadore, Ohio.

The mines are located at Mogadore, Summit County, on the W. & L. E. R. R. The sample, designated "D," was taken from a large pile of unweathered clay representing 15 rooms in the mine. A vertical section is as follows:

		Ft.	In.
Sample "D"	Shale, dark.....	6	0
	Coal, smutty.....	0	1
	Clay, siliceous, gray.....	4	6
	Shale, dark, argillaceous.....	1	0

Lower Kittanning Clay, Toronto, Ohio.

The lower Kittanning clay, designated "E," is from the mine of the Toronto Fire Clay Co., Toronto, Jefferson County, and was sampled under covering. The sample is a representative one from different rooms in the mine. A vertical section of the mine is as follows:

	Ft.	In.
Shale.....	15	0
Coal, Lower Kittanning.....	2	6
Sample "E" Clay (lower part siliceous).....	7	0
Clay, very siliceous, hard, gray...	5	0
Clay, bluish, sandy.....	2	0

Lower Kittanning Clays, New Brighton, Pa.

The clay, designated "F," was taken from a large pile of the Lower Kittanning clay at the Sherwood Bros. Pottery, New Brighton, Pa. This sample came from under cover and the section is similar to that at the mine of the A. F. Smith Co., both being Lower Kittanning clays occurring directly under the Lower Kittanning coal. The clay at the A. F. Smith Co. plant at New Brighton, is exposed and therefore is more weathered than that at the Sherwood Bros. Pottery. A vertical section of both mines is as follows:

	Ft.	In.
Coal, Lower Kittanning.....	0	1
Samples "F" and "G" Gray, plastic.....	5	0

Tionesta Clay, Crooksville, Ohio.

The sample designated "H," was taken from the mine of W. H. Brown and S. H. Sharky, located one mile west of Crooksville, Perry County. This clay is mined by drifting and is used extensively in both whiteware and stoneware potteries. The sample was taken from well under cover and from a clean face. The clay from this mine is shipped principally to the A. E. Hull Pottery. A vertical section is as follows:

	Ft.	In.
Shale.....	5	0
Limestone, Putman Hill.....	1	8
Coal, Brookville.....	0	4
Clay, light, plastic.....	6	0
Clay, dark, carbonaceous, horizon of Tionesta.....	0	2
Sample "H" Clay, light, plastic.....	6	0

Lower Kittanning Clay, Firebrick, Ohio.

The Lower Kittanning clay, designated "I," is used extensively in the manufacture of fire brick and sewer pipe in the southern

part of Lawrence County. The sample was taken from an open cut mine at Firebrick, Lawrence County. The bed is unusually free from nodules or sulphur compounds. A vertical section is as follows:

	Ft.	In.	
	8	0	
Sandstone.....	2	0	
Clay, shaly, Oak Hill.....	1	8	} Lower Kittanning
Coal.....	0	1 1/2	
Clay.....	0	8	
Coal.....	0	4	
Clay, dark, carbonaceous.....	5	0	
Sample "I" Clay, light, plastic.....	2	0	
Clay, siliceous, light.....			

Lower Kittanning Clay, Nelsonville, Ohio.

The Lower Kittanning clay, designated "J," is used extensively in the manufacture of brick at Nelsonville, Hocking County, and the sample was taken from the mine of the Hocking Valley Fire Brick Co., where it is used in the production of salt glazed building brick. A vertical section of the mine is as follows:

	Ft.	In.	
	x	0	
Sandstone.....	6	0	
Shale.....	1	8	
Coal, Lower Kittanning.....	0	4	
Clay, dark, carbonaceous.....	8	6	
Sample "J" Clay, light, plastic.....	5	0	
Sandstone, shaly.....			

Semi-flint Clay, Scioto Furnace, Ohio.

The semi-flint clay, designated "K," was taken from a large pile at the plant of the Buckeye Fire Brick and Clay Co., Scioto Furnace, Scioto County. The clay is used extensively in the manufacture of high grade fire brick. A vertical section of the mine is as follows:

	Ft.	In.	
	3	0	
Shale.....	0	1	
Coal, Anthony.....	2	0	
Clay, flint.....	1	6	
Sample "K" Clay, semi-flint, Sciotoville.....	2	0	
Clay, "pink eye".....			

INVESTIGATION.

For the purposes of the investigation test pieces were molded from seven bodies which were prepared from each of the stone-ware clays as follows:

Body No. 1—Run of mine clay ground dry to pass a 20-mesh sieve.

Body No. 2—Clay washed through a 150-mesh sieve.

Body No. 3—Residues from the washing were ground to pass a 150-mesh sieve and then added to the washed clay.

Body No. 4—95 per cent. washed clay (150-mesh) and 5 per cent. feldspar.

Body No. 5—90 per cent. washed clay (150-mesh) and 10 per cent. feldspar.

Body No. 6—95 per cent. washed clay (150-mesh) and 10 per cent. feldspar + 0.16 per cent. CaCO_3 .

Body No. 7—95 per cent. washed clay (150-mesh) and 5 per cent. feldspar + 6.1 per cent. CaCO_3 .¹

The drying shrinkage, water of plasticity, shrinkage water, pore water, rate of slaking in water, and the transverse strengths in the green condition were determined for each body.

The softening points of the clays were compared to those of Orton pyrometric cones. The apparent porosities and volume

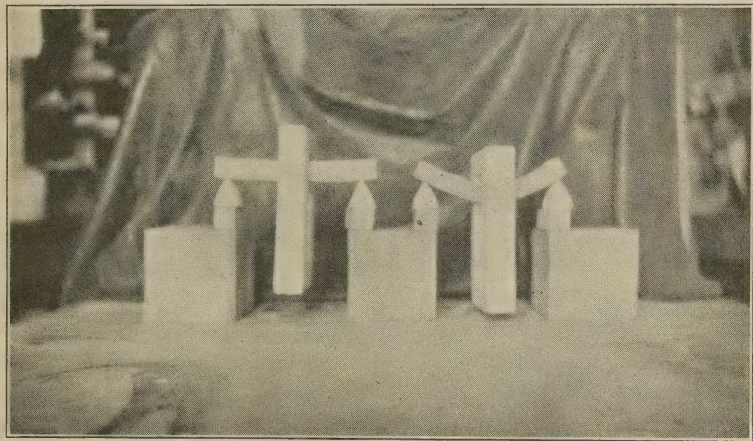


FIG. 1.—Clay bars before and after warpage test.

¹ Kirkpatrick, F. A., *Trans. Am. Ceram. Soc.*, **18**, 595 (1916). (The two calcite-orthoclase eutectics were used as a guide in adding the calcium carbonate.)

shrinkages of the briquettes were determined after firing to the different temperatures.

Owing to the fact that commercial chemical stoneware pieces are usually large, any tendency of the clays to warp, crack, or break in burning may cause high kiln losses. A modification of the warpage test as described by Worcester¹ was therefore employed—consisting in applying a load on the center of the

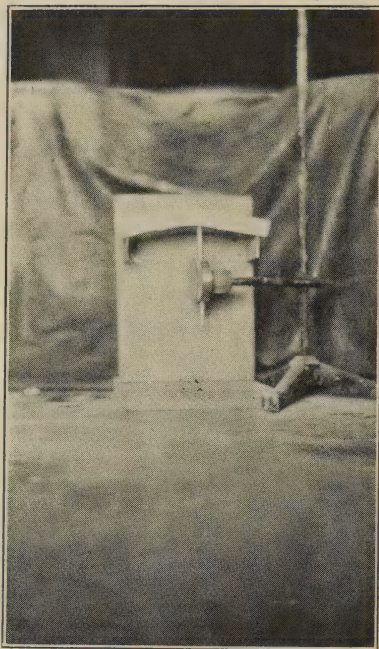


FIG. 2.—Method of measuring deformation with Ames dial.

test bars while resting upon two knife edges placed 6 inches apart, Fig. 1. A three-pound weight was applied to the bars having a 1" \times 1" cross section, corrections being made for those having a smaller cross section. The deformation (Fig. 2) was expressed in per cent. warpage in terms of the length of the span.

¹ Worcester, W. G., *Trans. Am. Ceram. Soc.*, 12, 818-853 (1910).

Transverse strength tests of the burned test bars were made after heating five times to 600° C and quenching in water at 18° C after each heating. The percentage decrease in strength gives a rough indication of the resistance of the fired bodies to temperature changes.

Results of the Tests.

Sample "A," Tionesta Clay, Ellis, Ohio.

This clay slakes down rapidly in water and is comparatively clean—leaving only 2.5 per cent. residue on the 150-mesh screen. It develops good mechanical strength in the raw and burned condition.

As all of the bodies investigated developed greater strength when burned to cone 8 than when burned to cones 6 or 10, it would appear that, for this class of clays and bodies, the maximum strength is developed by burning to cone 8. The difference in strength is probably due to underburning at cone 6 and overburning at cone 10. The strength of the clays and bodies is considerably increased by screening through the 150-mesh sieve.

The vitrification range is increased by screening through the 150-mesh sieve as compared with the run of mine clay screened through a 20-mesh sieve. The vitrification also starts about two cones lower. This is also true of the body in which the residue on the screen was ground to pass a 150-mesh sieve and then added to the washed clay. Screening the clay through a 150-mesh sieve also increases the burning shrinkage. Bodies Nos. 4, 5 and 6 have porosity and shrinkage curves which closely resemble that of the washed clay. Body No. 7 is comparatively open burning and has a short vitrification range. This is characteristic of high calcium bodies. The softening temperature is cone 26+ which roughly meets the requirements of a No. 3 fire clay as classified by Bleining.¹

The washed clay warps considerably under load. The run of mine clay, screened through the 20-mesh sieve, appears to be

¹ Bleining, A. V., "Some Aspects of the Testing of Refractories," *Proc. Eng. Soc. Western Penn.*, 32, 613 (1916).

more resistant to the quenching treatments than the same clay washed through a 150-mesh sieve.

Sample "B," Lower Kittanning Clay, Roseville, Ohio.

This clay slakes readily in water. Washing through a 150-mesh sieve affords a much "tighter" body than the run of mine clay screened through a 20-mesh sieve—as shown by a lower minimum porosity in the first case.

The softening point of this clay is cone 25+ and does not meet the requirements for a No. 1 fire clay. The clay warps considerably under load and therefore may be unsatisfactory if used alone.

Sample "C," Lower Mercer Clay, White Cottage, Ohio.

The clay does not slake readily in water and was therefore wet ground before blunging. The per cent. residue on a 150-mesh sieve is high. The strength of the raw clay is low while that of the burned clay is good. Adding the reground residue to the washed clay tends to open the body. The softening point, cone 26, would probably classify this material as a No. 2 fire clay. The warpage under load at cone 4 is excessive and high kiln losses may be expected if this clay is used alone in the manufacture of chemical stoneware.

Sample "D," Mogadore, Ohio.

This clay does not slake readily in water and was therefore wet ground before blunging. The per cent. residue on a 150-mesh sieve is high. The strength in the dry condition is low, although the burned strength is fair. The softening point is cone 18. The resistance of the test pieces, molded from the washed clay, to warpage under load, is not satisfactory.

Sample "E," Lower Kittanning Clay, Toronto, Ohio.

This clay does not slake in water and was therefore wet ground before blunging. The modulus of rupture of the test pieces from the washed clay is excellent while that of the clay when burned to cone 8 is also very good. The softening point is cone 26—roughly meeting the requirements for a No. 3 fire clay. The resistance to warpage under load is not very satisfactory.

Sample "F," Lower Kittanning Clay, New Brighton, Pa.

This clay slakes readily in water. The dry strength is low although the burned strength is fair. The softening point is cone 28—roughly meeting the requirements for a No. 2 fire clay. The resistance of the test pieces molded from the washed clay to warpage under load is poor.

Sample "G," Lower Kittanning Clay, New Brighton, Pa.

This clay slakes readily in water. The strength in the raw and burned condition is fair. The addition of the reground residue to the washed clay produces a more open body than the use of the washed clay alone. The softening point is cone 28, meeting the requirements for a No. 2 fire clay. The resistance to warpage under load at cone 4 is not satisfactory.

Sample "H," Tionesta Clay, Crooksville, Ohio.

This clay slakes readily in water. The dry strength is fair while the burned strength is good. The softening point is cone 28, which roughly meets the requirements of a No. 2 fire clay. The resistance to warpage under load is not very good.

Sample "I," Lower Kittanning Clay, Firebrick, Ohio.

This clay slakes readily in water. The strength in the dry and burned condition is excellent. The addition of feldspar to this clay is advisable as it widens and lowers the vitrification range by 4 cones. The color, when burned, is light gray and similar to that of the ball clays used in the manufacture of white ware. The softening point, cone 31, is sufficiently high to warrant the use of the clay in the manufacture of glass pots. The clay has only a small tendency to warp.

Sample "J," Lower Kittanning Clay, Nelsonville, Ohio.

This clay slakes readily in water. The per cent. residue remaining on the 150-mesh sieve is low. The strength in the dry and burned condition is excellent. The softening point, cone 30, classifies the material as a No. 2 fire clay. The resistance to warpage under load is fair.

Sample "K," Lower Kittanning Clay, Scioto Furnace, Ohio.

This clay does not slake readily in water and was therefore wet ground in a ball mill previous to blunging. The dry strength is low, although the burned strength is excellent. The softening point, cone 32+, classifies the material as a No. 1 fire clay. This clay is considered as being one of the typical fire-brick clays of Ohio. The resistance to cracking and warpage under load at cone 2 is very poor.

Summary.

With but few exceptions, the screening of the clays through a 150-mesh sieve improves the strength in the raw and burned condition, increases the dry porosity, lowers the vitrification temperature, widens the vitrification range, decreases the minimum burned porosity, increases the burning shrinkage, and increases the density in the burned condition.

When ground and screened to pass through a 150-mesh sieve, the residue from the washing may be added to the washed clay to advantage in most cases. The addition of feldspar alone or with a small percentage of calcium carbonate lowers the vitrification temperature. When a large percentage (6.1 per cent.) of calcium carbonate is added, the bodies are more porous at the lower temperatures, the vitrification temperature is raised, and in general the vitrification range is narrowed.

The maximum strength of all of the clays tested is developed by burning to cone 8.

There appears to be no relation between the softening temperature and the resistance to warpage under load at the low temperatures—the most refractory clays sometimes fail before the less refractory ones.

There is a large decrease in the mechanical strength when the clays are being burned above cone 1. In one case, the modulus of rupture was 270 in the dry state and, although the clay is a No. 1 fire clay, its modulus of rupture at cone 4 was decreased to 27.

The run of mine clays, screened dry through a 20-mesh sieve, appear to be more resistant to the quenching treatments than the same clays when screened through a 150-mesh sieve.

TABLE 1.—MISCELLANEOUS PROPERTIES.

No.	Per cent. residue on 150-mesh.	Per cent. porosity, dry.	Density, dry.	Modulus of rupture, lbs. per sq. in. (Dried 110° C).	Per cent. warpage.			Loss of strength due to quenching treatment. (Per cent.)	Softening points. (Cones.)
					Cone 1.	Cone 2.	Cone 4.		
1A.....	2.5	27.0	1.90	389.5	91.5	26+
2A.....	...	29.6	1.83	467.9	0.83	2.42	8.95	96.3	...
1B.....	6.1	23.8	2.06	218.6	77.5	26+
2B.....	...	28.1	1.87	319.5	2.77	5.13	9.99	97.7	...
1C.....	9.4	23.6	1.96	132.0	77.6	26
2C.....	...	25.7	1.80	250.7	2.75	6.10	15.10	93.0	...
1D.....	12.0	23.2	2.02	142.5	82.0	18
2D.....	...	28.5	1.87	259.0	1.80	3.48	6.40	93.0	...
1E.....	7.0	19.4	2.10	384.3	78.6	26—
2E.....	...	27.2	1.90	532.1	2.48	2.75	6.44	92.0	...
1F.....	9.4	23.4	1.99	194.2	82.5	28
2F.....	...	29.7	1.79	191.0	3.58	5.91	10.70	96.0	...
1G.....	12.5	24.5	1.94	194.5	83.5	28
2G.....	...	27.9	1.88	321.0	2.58	3.22	6.70	94.0	...
1H.....	7.2	23.1	1.98	178.8	73.5	28
2H.....	...	29.0	1.83	314.9	3.30	3.89	7.50	93.5	...
1I.....	1.2	24.8	1.89	324.9	85.5	31
2I.....	...	25.6	1.91	499.2	0.83	0.84	3.80	96.5	...
1J.....	3.4	20.8	2.04	247.3	77.5	30
2J.....	...	29.2	1.86	350.1	0.58	...	5.80	95.0	...
1K.....	5.0	18.5	2.03	93.8	55.5	32+
2K.....	...	28.4	1.88	270.0	0.58	8.85	broke	95.4	...

TABLE 2.—PER CENT. APPARENT POROSITIES OF CLAYS AND MIXTURES BURNED TO DIFFERENT TEMPERATURES.

No.	Cone 1.	Cone 2.	Cone 4.	Cone 6.	Cone 8.	Cone 10.	Cone 12.	Cone 14.
1A.....	19.38	15.90	3.70	0.78	0.93	0.20	2.20	...
2A.....	17.58	15.88	0.14	0.28	0.36	0.23	4.00	1.72
3A.....	19.28	16.10	0.14	0.21	0.36	0.16	1.50	1.59
4A.....	19.10	14.50	0.54	0.12	0.01	0.06	3.90	2.47
5A.....	19.05	14.65	0.14	0.17	0.08	0.09	0.35	3.70
6A.....	18.80	14.10	0.03	0.06	0.15	0.00	0.16	3.46
7A.....	24.85	19.80	6.49	1.07	5.99	...	5.70	3.39

TABLE 2.—(Continued).

No.	Cone 1.	Cone 2.	Cone 4.	Cone 6.	Cone 8.	Cone 10.	Cone 12.	Cone 14.
1B.....	18.93	17.15	12.99	12.79	12.48	14.80	12.80	5.20
2B.....	20.60	14.15	0.91	0.24	4.97	3.20	6.30	...
3B.....	21.45	14.60	0.24	0.94	3.99	1.04	6.80	...
4B.....	16.75	15.50	0.34	0.15	2.03	0.78	4.60	4.35
5B.....	17.50	14.65	0.12	0.12	4.77	0.60	6.40	...
6B.....	17.15	14.28	0.99	0.24	2.21	2.18	5.00	...
7B.....	23.15	23.15	15.90	6.00	0.28	0.00	5.50	...
1C.....	19.60	22.80	14.55	10.40	7.32	4.95	5.10	8.50
2C.....	19.90	18.50	6.59	2.75	0.78	1.45	6.10	8.31
3C.....	24.00	24.10	12.65	9.00	1.31	4.41	6.70	9.68
4C.....	21.55	21.35	10.25	4.30	1.93	2.34	3.60	8.72
5C.....	22.00	18.35	9.70	4.60	2.09	1.54	6.00	6.50
6C.....	22.05	21.25	10.33	3.75	0.59	2.94	6.00	7.40
7C.....	28.63	29.20	18.10	8.00	0.22	0.00	7.00	...
1D.....	24.75	25.25	18.80	15.30	12.12	7.33	4.80	5.65
2D.....	22.55	23.60	17.50	9.40	3.63	3.37	3.37	11.70
3D.....	27.48	26.30	19.00	10.60	2.92	2.75	6.20	10.48
4D.....	23.15	23.55	16.20	4.30	2.93	2.17	8.60	10.20
5D.....	24.35	22.30	7.73	7.50	2.49	2.29	9.80	6.12
6D.....	22.85	22.85	9.33	8.88	2.44	1.55	9.00	7.37
7D.....	29.05	30.30	14.23	11.53	9.35	9.30	19.00	...
1E.....	22.20	19.75	10.74	10.88	10.93	10.51	11.00	10.70
2E.....	24.30	20.25	7.43	4.00	3.25	7.80	8.80	8.72
3E.....	24.70	19.83	6.50	3.00	2.21	6.95	8.50	10.40
4E.....	24.90	20.55	8.60	2.50	0.23	11.70	6.20	...
5E.....	21.20	17.60	5.98	1.00	5.69	5.82	9.20	...
6E.....	24.80	21.00	11.69	4.50	2.46	12.10	6.30	2.41
7E.....	23.65	23.15	14.25	5.75	0.06	0.00	7.90	8.20
1F.....	20.20	23.40	16.58	14.25	13.24	12.45	7.50	2.44
2F.....	24.95	25.05	11.00	3.75	1.03	5.57	6.40	6.68
3F.....	25.60	27.00	13.70	5.40	3.31	3.71	5.10	5.58
4F.....	21.90	24.55	7.89	4.00	2.58	6.88	10.30	3.00
5F.....	23.55	25.20	6.36	4.00	4.44	4.88	9.80	2.77
6F.....	20.75	24.30	8.33	2.50	0.29	1.84	3.50	2.90
7F.....	27.35	31.65	14.35	4.00	0.08	0.28	1.70	...
1G.....	21.95	22.95	20.00	15.00	10.32	9.60	5.20	10.85
2G.....	21.35	19.85	16.00	5.00	1.80	7.49	8.00	11.20
3G.....	23.00	21.95	18.00	8.75	3.02	5.60	7.10	12.60
4G.....	21.00	18.75	14.00	2.80	0.39	0.26	4.10	10.90
5G.....	22.30	18.95	14.00	4.00	1.15	5.23	6.60	5.09
6G.....	24.00	21.20	12.50	5.00	0.73	6.55	8.10	11.45
7G.....	27.00	26.70	15.95	4.00	0.33	0.18	9.40	...

TABLE 2.—(Continued).

No.	Cone 1.	Cone 2.	Cone 4.	Cone 6.	Cone 8.	Cone 10.	Cone 12.	Cone 14.
1H.....	24.95	22.95	17.80	16.00	14.50	11.40	10.00	5.48
2H.....	26.75	22.00	16.20	5.50	0.25	3.30	0.59	7.95
3H.....	25.00	19.10	14.58	10.60	6.68	4.14	1.79	2.42
4H.....	25.65	21.20	7.85	2.00	0.37	0.00	4.20	...
5H.....	22.75	18.00	7.98	1.75	0.41	0.17	5.30	7.56
6H.....	24.00	21.20	10.23	2.50	0.35	0.29	0.59	6.31
7H.....	27.00	26.70	15.95	4.50	0.29	0.24	0.78	...
1I.....	19.15	19.10	16.23	12.00	10.78	7.84	6.30	6.64
2I.....	18.23	19.40	11.95	7.25	5.23	4.55	0.17	8.50
3I.....	19.65	19.10	12.55	7.75	5.54	4.74	1.30	8.90
4I.....	18.30	17.55	9.29	3.75	0.61	0.45	1.80	5.04
5I.....	14.48	13.40	5.89	1.90	0.08	0.01	2.70	3.91
6I.....	16.20	15.30	10.10	4.75	0.33	1.15	0.49	4.52
7I.....	16.70	14.65	13.27	8.50	3.22	0.12	0.00	9.10
1J.....	21.75	18.95	15.01	12.10	10.66	10.45	8.30	...
2J.....	24.20	21.75	12.40	3.00	0.08	0.43	1.06	5.77
3J.....	24.95	21.55	12.30	4.75	0.23	0.32	3.60	8.71
4J.....	22.80	18.20	10.70	2.60	0.09	0.19	0.73	7.43
5J.....	22.85	17.30	9.80	2.25	0.09	0.12	3.30	7.85
6J.....	22.90	18.70	9.60	2.25	0.09	0.13	3.31	7.40
7J.....	27.00	27.15	17.45	7.00	0.12	0.05	0.02	10.70
1K.....	23.85	20.85	22.50	22.80	21.65	19.10	17.20	18.15
2K.....	21.65	18.55	14.07	9.75	8.70	8.40	2.30	2.85
3K.....	25.30	19.65	18.73	12.50	11.25	10.70	5.25	3.57
4K.....	22.90	16.15	12.98	9.00	6.65	5.67	1.60	3.42
5K.....	21.70	14.50	11.66	7.50	2.95	1.49	4.72	1.90
6K.....	20.55	15.30	9.53	8.00	6.47	5.38	0.00	1.81
7K.....	16.35	17.25	15.65	12.00	10.14	8.82	0.15	1.53

TABLE 3.—MODULUS OF RUPTURE OF BURNED BODIES.

No.	Cone 6.	Cone 8.	Cone 10.
1A.....	4624.0	6680.0	3812.0
2A.....	7200.0	8265.0	5330.0
3A.....	7240.0	10747.0	4671.0
4A.....	6538.0	7780.0	4910.0
5A.....	6540.0	6787.0	5966.0
6A.....	6616.0	8728.6	6001.0
7A.....	5566.0	6958.3	5779.0

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TABLE 3.—(Continued).

No.	Cone 6.	Cone 8.	Cone 10.
1B.....	3190.0	3416.2	2665.0
2B.....	8556.0	8680.0	7504.8
3B.....	7628.0	9505.0	9462.0
4B.....	8130.0	9738.3	6911.6
5B.....	7010.0	8482.9	7050.0
6B.....	6957.0	7514.0	6494.0
7B.....	5434.0	6003.7	4853.0
1C.....	2964.0	3223.7	1670.0
2C.....	5703.0	7285.0	4681.0
3C.....	4534.0	6485.0	4543.0
4C.....	5254.0	5843.7	4421.0
5C.....	5491.0	7802.5	4749.0
6C.....	4564.0	5090.0	4321.0
7C.....	4090.0	7067.1	3464.0
1D.....	2023.0	2283.7	2181.0
2D.....	4666.0	4820.0	3361.0
3D.....	3686.0	4585.0	2418.0
4D.....	4284.0	5581.4	3326.0
5D.....	4621.0	5790.0	2991.0
6D.....	4606.2	5877.5	3944.0
7D.....	3944.3	4627.5	2218.0
1E.....	2788.7	3568.7	2260.0
2E.....	7904.3	6847.5	5690.0
3E.....
4E.....	5882.8	6397.5	5084.0
5E.....	5128.6	5191.6	4584.0
6E.....	5430.0	5588.5	4155.0
7E.....	5168.7	5385.0	4873.0
1F.....	2911.2	3063.0	1909.0
2F.....	4932.5	5815.0	3368.0
3F.....	4213.8	5133.0	3750.0
4F.....	4472.5	5507.0	3869.0
5F.....	6275.0	6727.0	2675.0
6F.....	4751.4	6059.0	3260.0
7F.....	3908.7	5309.0	2057.0
1G.....	2580.0	3288.7	1521.0
2G.....	5113.0	5183.7	4474.0
3G.....	4948.7	6350.0	2643.0
4G.....	4993.8	5473.0	5400.0
5G.....	4853.7	6284.0	4506.0
6G.....	4973.0	5780.0	4381.0
7G.....	3715.0	5890.0	4545.0

TABLE 3.—(Continued).

No.	Cone 6.	Cone 8.	Cone 10.
1H.....	1974.0	3043.7	1956.0
2H.....	6615.0	7148.7	3689.0
3H.....	2873.3	6837.0	1912.0
4H.....	5682.0	7960.0	4586.0
5H.....	6111.2	9075.0	3941.0
6H.....	6591.2	7768.5	5535.0
7H.....	5058.7	6208.7	3682.0
1I.....	4068.7	5075.0	3014.5
2I.....	10448.3	7190.0	6175.6
3I.....	9438.0	6073.0
4I.....	7045.0	9691.0	7023.0
5I.....	6734.0	7227.5	7207.0
6I.....	6847.1	8837.1	7238.0
7I.....	5561.0	6052.9	5169.0
1J.....	1569.0	3507.5	2034.0
2J.....	4699.0	6150.0	5004.0
3J.....	5619.0	6522.5	4125.0
4J.....	5523.0	8640.0	4018.0
5J.....	6404.0	6635.0	5799.0
6J.....	6165.0	8481.2	5850.0
7J.....	5561.4	6221.1	4528.0
1K.....	1649.4	2129.3	2041.0
2K.....	3655.0	7411.0	2716.0
3K.....	3730.0	8976.0	3201.0
4K.....	2836.6	5742.0	3546.0
5K.....	3585.0	4710.0	3567.0
6K.....	2235.0	8740.0	2046.0
7K.....	2437.8	5621.2	5064.0

TABLE 4.—PER CENT. VOLUME SHRINKAGE OF CLAYS AND MIXTURES BURNED TO DIFFERENT TEMPERATURES.

No.	Cone 1.	Cone 2.	Cone 4.	Cone 6.	Cone 8.	Cone 10.	Cone 12.
1A.....	13.20	15.90	24.00	24.31	23.30	24.90	...
2A.....	19.80	21.10	29.55	29.50	28.80	29.10	21.80
3A.....	20.90	22.05	30.85	32.25	32.35	32.55	28.10
4A.....	17.95	20.83	28.09	30.25	35.60	28.00	...
5A.....	17.53	*19.35	27.41	28.75	28.85	28.85	25.80
6A.....	21.15	23.80	30.64	31.60	31.45	31.55	28.50
7A.....	13.85	14.85	24.44	23.51	17.20	...	22.90

TABLE 4.—(Continued).

No.	Cone 1.	Cone 2.	Cone 4.	Cone 6.	Cone 8.	Cone 10.	Cone 12.
1B.....	14.40	14.70	17.12	16.53	9.06	8.63	6.30
2B.....	20.45	25.05	32.30	31.19	24.80	...	41.25
3B.....	21.85	25.65	32.40	34.58	26.60	...	33.95
4B.....	19.75	22.60	29.00	28.73	26.80	...	22.20
5B.....	15.10	20.65	27.13	27.48	22.40	22.80	27.20
6B.....	20.00	22.45	29.18	28.80	24.15	...	31.60
7B.....	14.50	15.80	19.24	21.70	24.80	...	24.60
1C.....	7.43	8.36	15.14	16.25	16.40	16.40	13.70
2C.....	16.15	20.25	26.75	27.95	28.40	26.80	19.35
3C.....	10.08	13.89	20.88	26.65	28.40	23.80	20.60
4C.....	12.60	14.87	22.10	24.25	24.85	24.65	23.75
5C.....	12.83	18.00	18.50	25.36	23.55	23.10	17.30
6C.....	12.23	15.12	20.70	24.25	27.35	23.40	19.50
7C.....	6.10	7.66	16.15	22.50	25.75	25.90	14.30
1D.....	3.70	5.98	6.92	7.95	9.00	10.90	14.10
2D.....	8.43	8.64	17.85	18.96	23.45	23.40	19.80
3D.....	5.86	8.51	18.13	20.75	24.90	25.00	20.50
4D.....	8.18	9.36	17.48	18.30	23.40	23.40	14.50
5D.....	8.55	10.98	19.38	20.95	22.4	22.30	5.40
6D.....	8.33	7.82	16.53	19.00	23.65	23.60	9.00
7D.....	2.93	3.54	15.03	19.95	21.97	20.03	19.00
1E.....	7.14	8.60	15.03	9.43	6.06	5.57	4.60
2E.....	10.64	15.87	23.50	22.70	21.90	20.60	15.90
3E.....	10.85	15.21	24.80	24.65	24.80	22.40	17.60
4E.....	11.55	14.65	22.85	24.00	25.55	23.00	20.30
5E.....	14.40	15.47	24.55	25.70	20.35	18.30	14.10
6E.....	10.45	14.19	21.88	23.65	23.35	...	16.75
7E.....	10.02	13.56	14.28	16.78	23.00	23.50	13.30
1F.....	3.64	5.92	8.25	9.42	12.43	11.95	7.50
2F.....	9.23	12.85	19.00	22.00	28.65	22.93	3.40
3F.....	8.10	11.36	16.25	20.00	28.25	27.75	5.10
4F.....	11.28	14.03	20.00	25.69	24.40	19.20	10.30
5F.....	9.23	13.96	20.00	26.38	22.15	20.25	9.80
6F.....	9.78	13.17	13.25	24.65	28.15	27.80	3.50
7F.....	5.93	8.28	12.00	20.03	23.45	29.40	1.70
1G.....	6.48	7.37	14.00	14.40	17.50	20.20	18.00
2G.....	9.49	16.74	20.20	24.00	26.60	23.00	20.60
3G.....	8.53	9.93	18.10	24.30	25.90	23.45	23.20
4G.....	9.73	14.96	20.55	24.00	26.55	22.95	16.33
5G.....	11.68	15.63	24.30	26.00	25.40	22.70	15.45
6G.....	10.78	14.50	21.70	26.60	26.85	22.00	18.45
7G.....	5.59	8.05	17.65	22.75	25.40	25.55	12.40

TABLE 4.—(Continued).

No.	Cone 1.	Cone 2.	Cone 4.	Cone 6.	Cone 8.	Cone 10.	Cone 12.
1H.....	6.63	8.32	11.35	13.00	13.70	13.43	13.10
2H.....	13.88	16.52	23.55	23.00	28.55	33.40	...
3H.....	15.00	16.68	29.70	32.00	32.85	33.00	34.00
4H.....	12.70	16.36	25.35	26.40	27.10	27.30	21.00
5H.....	13.45	18.54	25.00	27.30	26.80	27.00	19.00
6H.....	13.55	16.87	23.00	27.00	28.80	28.85	28.60
7H.....	9.60	11.44	18.15	25.00	28.20	28.20	24.80
1I.....	13.63	15.03	16.80	19.60	20.40	20.65	22.00
2I.....	17.75	19.40	22.30	25.00	25.75	25.95	26.40
3I.....	17.53	17.71	21.55	22.00	22.00	22.70	27.80
4I.....	14.30	16.38	21.00	24.00	24.25	22.80	...
5I.....	19.17	21.40	24.20	25.70	26.25	28.60	15.00
6I.....	19.10	20.98	24.05	27.00	28.15	27.70	...
7I.....	9.60	11.44	18.15	22.50	24.60	26.90	22.90
1J.....	9.78	10.96	13.30	12.10	10.10	10.10	7.50
2J.....	13.73	16.40	22.45	29.00	30.10	29.90	28.90
3J.....	14.90	16.91	22.80	28.50	29.70	29.00	23.70
4J.....	13.60	18.23	23.55	29.00	30.45	30.40	28.00
5J.....	15.50	18.55	24.00	28.10	29.25	29.50	21.10
6J.....	15.90	17.84	25.15	29.50	30.30	31.90	25.60
7J.....	7.32	8.45	14.50	22.00	26.10	26.30	25.50
1K.....	15.40	16.59	18.40	20.25	20.90	18.88	17.10
2K.....	23.05	25.15	28.90	31.25	32.00	32.30	33.40
3K.....	21.40	23.28	24.90	27.50	30.45	30.85	33.55
4K.....	22.75	27.63	30.10	32.00	33.55	34.15	35.60
5K.....	23.20	28.78	30.10	32.00	34.10	34.75	35.30
6K.....	20.80	26.18	28.20	30.50	32.15	32.60	34.00
7K.....	...	23.70	23.80	26.00	28.30	28.50	30.15

TABLE 5.—SHRINKAGE RELATIONS.

No.	Description.	Per cent. total water in terms of true clay volume.	Per cent. shrinkage water in terms of true clay volume.	Per cent. pore water in terms of true clay volume.	Ratio of per cent. pore water to per cent. shrinkage water.	Per cent. shrinkage water in terms of total water.	Per cent. water of plasticity in terms of dry weight.	Per cent. volume shrinkage in terms of dry volume.
1A	Run of mine.....	78.8	41.7	37.3	0.92	52.9	30.3	30.5
2A	Washed.....	83.9	44.0	39.9	0.91	52.4	34.2	33.2
1B	Run of mine.....	71.3	40.3	31.0	0.77	56.5	27.5	30.8
2B	Washed.....	90.6	48.5	42.1	0.87	53.5	34.8	33.0

TABLE 5.—(Continued).

No.	Description.	Per cent. total water in terms of true clay volume.	Per cent. shrinkage water in terms of true clay volume.	Per cent. pore water in terms of true clay volume.	Ratio of per cent. pore water to per cent. shrinkage water.	Per cent. shrinkage water in terms of total water.	Per cent. water of plasticity in terms of dry weight.	Per cent. volume shrinkage in terms of dry volume.
1C	Run of mine.....	61.1	30.2	30.9	1.02	49.5	23.5	22.9
2C	Washed.....	81.6	38.3	43.3	1.13	46.9	31.4	26.6
1D	Run of mine.....	49.8	20.8	29.0	1.40	41.7	19.1	16.1
2D	Washed.....	75.0	37.1	37.9	1.02	49.5	28.9	26.7
1E	Run of mine.....	49.0	23.5	25.5	1.07	48.0	18.9	18.9
2E	Washed.....	86.3	50.5	35.8	0.71	58.5	33.2	36.2
1F	Run of mine.....	54.6	26.0	28.6	1.19	47.5	21.0	20.0
2F	Washed.....	83.8	38.8	45.0	1.16	46.3	32.2	26.4
1G	Run of mine.....	64.5	33.7	30.8	0.91	52.2	24.8	25.1
2G	Washed.....	76.0	39.8	36.2	0.91	52.3	29.2	27.4
1H	Run of mine.....	63.1	29.8	33.3	1.12	47.1	24.3	22.7
2H	Washed.....	88.0	46.0	42.0	0.91	52.3	33.8	32.3
1I	Run of mine.....	88.5	56.0	32.5	0.58	63.3	34.2	40.6
2I	Washed.....	89.6	55.6	34.0	0.61	62.0	34.6	41.2
1J	Run of mine.....	59.6	30.6	29.0	0.95	51.3	23.0	22.7
2J	Washed.....	87.6	48.5	39.1	0.81	55.4	33.7	34.7
1K	Run of mine.....	43.5	17.8	25.7	1.44	41.0	16.8	14.0
2K	Washed.....	86.0	48.0	38.0	0.79	55.8	33.1	34.6

The properties of the above Ohio and Pennsylvania stoneware clays were studied by the Bureau of Mines under the direction of Prof. A. S. Watts in coöperation with the Ohio Geological Survey. The Pennsylvania Geological Survey also assisted in obtaining the Pennsylvania stoneware clay samples. Although this work was done with special reference to chemical stoneware, many results were brought out which may be applied to a number of other ceramic industries.

THE USE OF DENSE SOLUTIONS IN DETERMINING THE STRUCTURE OF PORCELAINS.

By H. SPURRIER, Detroit, Mich.

Petrographers and mineralogists have used dense organic and inorganic solutions for a number of years in the separation of minerals having different specific gravities. Under certain conditions fused solids have also been used.

The use of a dense solution in the grading of porcelains was suggested by the variations in specific gravity encountered in underfired, properly fired and overfired spark plug insulators. A slightly underfired piece of porcelain has a higher specific gravity than a properly fired piece of the same composition while the specific gravity of an overfired piece is less than that of a properly fired piece.

In an attempt to determine the reliability and accuracy of a visual inspection of porcelains the following tests were made:

Four pieces of porcelain were selected and visually classified by a competent inspector. Two of the pieces were rejected by him as being overfired and two were passed as being properly fired. However, one of the pieces selected as being properly fired showed a tendency toward slight overfiring. Upon submitting the same four pieces to another inspector, he classified them in the same way, confirming the judgment of the first inspector.

Careful specific gravity determinations on the four pieces gave the following results:

Classification (inspector).	Sp. Gr.
Overfired.....	1.865
“.....	1.861
Properly fired.....	2.086
“.....	1.916

The piece having a specific gravity of 1.916 was the one in regard to which there was a slight question as to its being properly

fired. It is apparent, therefore, that visual examination by skillful inspectors is not all that could be desired in the selection of the properly fired porcelains.

For the rapid laboratory or factory testing of porcelains by means of heavy solutions, a liquid having the following properties is necessary:

1. The specific gravity should be 2.3 or above.
2. The liquid should be mobile at the necessary concentrations.
3. It should not exert a corrosive action on the material being tested.
4. It should be fairly constant in specific gravity.
5. It should be available in commercial quantities at reasonable cost.

In endeavoring to find a liquid which would be suitable for the specific-gravity determinations on porcelains, the following observations were made in reference to some of the solutions used by mineralogists:

Acetylene tetrabromide can be diluted only with ether or benzol and is therefore somewhat unstable as to specific gravity.

Methylene iodide is easily decomposed by light.

Klein's solution, cadmium borotungstate, is prepared with considerable difficulty.

The specific gravity of concentrated zinc chloride (82.12 per cent. ZnCl_2 , 17.88 H_2O) is 2.2307. At the desired concentration, however, it is quite viscous.

Potassium mercuric iodide meets all of the requirements of a liquid to be used for this purpose but is quite expensive.

Acid nitrate of mercury is quite mobile and remarkably stable and appears to have all of the desirable properties enumerated above.

In the grading of porcelains in our laboratory by means of the acid mercuric nitrate, two solutions are used, the one being diluted so as to just float a properly fired piece and to allow an under-fired piece to sink—the other being so diluted as to allow a properly fired piece to sink and an overfired piece to float. The solutions may become a little too dense with age but this is remedied by the addition of a little water acidified with nitric acid.

The density of the solution, when once established for a certain body, should be checked from time to time by means of a good specific gravity hydrometer. Upon removing and washing the tested pieces with water, a yellow deposit will occur but this can be easily removed with a little acetic acid.

It is, of course, quite obvious that the specific gravity of fired ware may vary quite sensibly in consequence of the presence of mechanical voids, and that a properly fired piece of ware may possess an apparent specific gravity below the established standards. In such cases the ware is rejected by the solution. This is as it should be where careful selection of the porcelains is necessary. The fact that invisible imperfections in the porcelains are at once detected by this method makes it more efficient than visual examination by the inspector.

We have used a solution of the acid mercuric nitrate only as a rapid laboratory check for the insulator inspectors but its use offers interesting possibilities as an exact method for factory testing.

By the employment of this method, one more operation is relieved of the uncertain personal factor and placed upon an unvarying mathematical basis.

JEFFERY-DEWITT Co.,
DETROIT, MICH.

DISCUSSION.

MR. McDUGAL: I would like to ask Mr. Spurrier if he has found that a difference in the thickness of the glaze on a spark plug insulator would be an important factor in the employment of this test; that is, would a heavier glaze on one piece affect the apparent specific gravity so as to indicate an apparently denser structure than that of a piece having a lighter glaze coating?

MR. SPURRIER: A glaze usually has a higher specific gravity than the body to which it is applied, and if the glaze area is very large, in proportion to the volume of the porcelain, it will be a source of error in the specific gravity determination. The glaze, if uniform, is usually so thin that, within the necessary limits, it does not affect the behavior of the piece in the solution.

MR. CREIGHTON: This method, in its simplicity, appeals to me very greatly. I should like to ask Mr. Spurrier if the size of the piece is not an important factor to be considered, and also if the character of the surface of the piece, whether rough or smooth, will not affect the results? If the surface of the piece is rough, will not a certain amount of air be trapped when the piece is dropped into the solution—thus affecting the reading? If the piece is large the importance of this factor would be diminished.

MR. SPURRIER: In making specific-gravity determinations in water great care is necessary to prevent the entrapping of air by the piece being tested. I have found, however, that by exercising reasonable care, no difficulties from entrapped air are encountered in the testing of the porcelain pieces in the dense solutions.

MR. WATTS: I would like to ask Mr. Spurrier whether—in the use of these solutions—there would be any objection to placing the porcelains in a metal gauze basket while inserting into the solutions? Are the solutions corrosive to metals—nickel, etc.?

MR. SPURRIER: Yes, the dilute nitric acid, but some of the high silica irons now available are particularly resistant to nitric acid and the mercury does not affect them.

MR. WATTS: That is just the point I wanted to raise: would a small amount of the metal that might be taken up from the basket materially affect the density of the solution?

MR. SPURRIER: No, I think not, because the volume of the liquid is large in proportion to the volume of the pieces being tested.

JOURNAL

OF THE

AMERICAN CERAMIC SOCIETY

A monthly journal devoted to the arts and sciences related to the silicate industries.

Vol. 1

May, 1918

No. 5

EDITORIALS.

CHEMICAL STONEWARE.

The manufacture of chemical stoneware has been greatly influenced and stimulated by the demands of the war and the importance of this product in the manufacture of certain war essentials, such as acids, heavy chemicals, high explosives, medicines, etc., has proven second to no other product. In the new and important industry of the fixation of atmospheric nitrogen, which the Government is developing upon such an enormous scale, chemical stoneware will play an important and leading role. Chemical stoneware is used on a large scale in the production of picric acid and of nitric acid. Perhaps no development of the war holds as much popular and scientific interest as the production of poison gases and gas shell. Here again chemical stoneware is necessary to large scale production and without it the manufacture of this new war essential would be greatly handicapped.

When we consider that chemical stoneware really takes the place of chemical glassware in large scale production, its uses and necessary properties are better understood. In the laboratory the chemist uses chemical glassware for his work but the use of chemical glassware in factory operations is out of the question. Here, chemical stoneware enters and its manufacture into the complicated shapes required is little short of wonderful. In order that it may stand up under factory conditions—which may include corrosion, high temperatures, high pressures, and rapid

heating and cooling—the quality and construction of the ware must be of the very highest grade.

The entire system of an acid plant is often made from this ware. Starting from the still, all of the pipes, cooling coils, pumps, elevators, containers, towers, condensers and collectors are so constructed that the acid is in contact only with acid-proof stoneware throughout the system. The automatic acid pumps have valves and pistons of stoneware—ground to fit accurately. The exhausters have stoneware casings, propellers and driving shafts—accurately fitted with ground joints. To complete the cycle, the acid will soon be conveyed to the consumer in chemical stoneware carboys.

Before the war, it was generally believed that the best stoneware could be made only in Germany—where the development of the industry had received much care and attention. Some of the highest grade stoneware on the market in this country at that time was made from raw clay bodies imported from Germany. With the outbreak of the war, however, it became necessary to develop sources of raw materials and this has been done to a highly successful degree. At the present time it may be stated that there is being produced in this country chemical stoneware which is superior in every respect to any made in Germany previous to the war. The manufacturers of this essential product have met the increased war demands in splendid style and all requirements have been quickly met. Chemical stoneware will undoubtedly continue to play a leading rôle in our greatly expanded chemical industry.

THE AMERICAN CERAMIC SOCIETY AND THE WAR.

It is gratifying to note that the American Ceramic Society, through the efforts of its War Service Committee, has received recognition by the War Industries Board through the appointment of Homer F. Staley, President of the Society, as Technical Advisor in Ceramics to the Board. Mr. Staley will cooperate with the other members of the staff dealing with the problems arising in the production of such ceramic products as optical glass, chemical stoneware, tableware, chemical porcelain, building

materials, and the production and importation of white-burning clays.

The importance of ceramic products in the manufacture of a great many of the war essentials is unquestioned. Up to this time our members have individually and collectively given their services toward the solution of the many war problems arising in the industry but there has been a serious lack of team-work and coöperation. Mr. Staley's appointment as Technical Advisor to the War Industries Board fills a long-felt want and gives to the American Ceramic Society, the one great technical society representing a large and very essential industry, the recognition it deserves.

WAR CURRICULUM IN CERAMIC ENGINEERING

It is interesting to note that the Committee on Ceramic Chemistry of the National Research Council is now preparing a War Curriculum in Ceramic Engineering for those Colleges and Universities maintaining units of the Student Army Training Corps and having Departments of Ceramic Engineering. After consultation with the Ceramic Departments involved, a tentative curriculum has been agreed upon and courses in this branch of engineering will be afforded. The Curriculum in Ceramic Engineering as outlined includes most of the courses now offered. However, special courses in Combustion and Fuel Engineering are notable additions. It is to be hoped that a sufficient number of the students will take advantage of the Ceramic Engineering courses so that the future demand for technically trained Ceramic Engineers will be supplied.

ORIGINAL PAPERS AND DISCUSSIONS.

A STUDY OF DRAFT MOVEMENTS IN FLUES.

By EDWIN H. FRITZ, Derry, Pa.

Introduction.

In a paper by C. B. Harrop¹ on "The Inadequacy of Static Pressure Draft Gages," he proved beyond question that the ordinary draft gage is apt to be misleading, and that its readings do not indicate the rate of movement of gases in the kiln because the pressure, producing this movement, is entirely different from the static pressure measured by the draft gage. The pressure causing the rate of movement or velocity of flow of gases is called the "velocity pressure" and when added to the static pressure—which is the pressure required to overcome the resistance offered to the flow—gives the total pressure or draft intensity of a stack. The "velocity pressure" is not apt to vary directly with the static pressure and for this reason cannot be equal to it. Therefore, if the static pressure reading, as obtained by a draft gage, is assumed to be the velocity pressure, the results will be erroneous.

As an illustration, Harrop discussed a stack having a grate bar furnace built into its base, and with the internal gases at a temperature of 600° F. If the fire and ash doors were closed, the draft intensity was 0.6 inch (water column). If the ash doors were opened and the friction in the chimney was considered as negligible, a velocity pressure of 0.3 inch was developed. At the same time, the draft gage would show a reading of 0.3 inch over the grates. Assuming a constant stack temperature and a thicker fuel bed offering 50 per cent. more resistance to the passage of the air—only three-fourths as much air would pass through and the corresponding velocity pressure would be less than before. The draft gage

¹ *Trans. Am. Ceram. Soc.*, 18, 223 (1916).

recording the static pressure, or the difference between the total draft intensity and the velocity pressure, would read higher. Thus he pointed out that by thickening the fuel bed and, therefore, by decreasing the volume of gas flowing through the grates, the draft gage gave a higher reading. This higher reading would erroneously indicate a better draft.

Investigation.

It seems that the inconsistency and tendency of the draft gages to mislead is not quite generally known and as there are many in actual use the necessity for a better method for its use is evident. Accordingly, this investigation was undertaken with a view to either finding a way to make the draft gage indicate the rate of movement of the gases or to find some other way of measuring the volume of gas passing through a flue.

The method selected was that suggested by Harrop¹ at the close of his paper and also mentioned in the discussion of his paper. Briefly, the measurement of the static pressure between two points in a flue was taken as a basis—the friction between the two points always being constant with any given velocity of gases.

The apparatus used consisted of static pressure tubes inserted into a flue at the two points and each connected to one end of a U-tube, as used on the draft gage. A differential reading giving the friction between the two points was then taken. As long as no air passes through the flue, there is no friction and consequently the liquid in both tubes would stand at the same level. However, as soon as air passes through, there is friction and this friction would be measured by the differential reading on the gage. It is evident that the differential reading would vary directly as the volume of gas passing through the flue, since the greater the volume the greater the velocity of the gas and the greater, therefore, the resistance offered by the flue. However, since the velocity of the gas in the flue between a kiln and stack is only about 600 feet per minute, the two points in the flue would have to be a great distance apart in order to get an appreciable reading—a straight flue offering but little resistance. In fact, the full length of most kiln

¹ *Trans. Am. Ceram. Soc.*, 18, 223 (1916).

flues would be too short to give sufficient resistance. It was therefore necessary to devise a different method for providing this resistance.

Apparatus.

The use of a diaphragm with an orifice, as used by the Bailey Meter Company and others in their flow meters, used primarily for the measurement of steam and water pressure, was thought especially desirable. There appeared to be no reason why this method could not be made applicable in the measurement of the amount of gas flow in a flue system. It has been found to be extremely accurate by the Bailey Meter Company in their meters and preferable to the Pitot tube.

The Pitot Tube.

The Pitot tube is not suitable for measuring the flow of gases at the low velocities usually found in flues and requires long runs of straight flow before it will give accurate results. It is also difficult to get an average reading with the Pitot tube, especially when the cross section of the flue is irregular. The latter disadvantage would undoubtedly be met in kiln flues, for the flue between kiln and stack is often quite short and since a straight flue is needed on both sides of the tube, this instrument would hardly be practical. Besides, it must be used very carefully in order to get accurate results. Therefore, the use of a diaphragm with orifice in a flue, if it could be made applicable, seemed to be the most practical.

Experimental Flue.

It was considered inadvisable to carry on the experimental work with a flue connected to a stack because no means of controlling the draft and of testing different sized flues were available. An electrically driven fan was therefore connected at its inlet to a wooden flue (Fig. 1) thus producing an induced draft. The wooden flue was $35'' \times 35'' \times 12'$ in length and was made as air-tight as possible. It had but three sides, the concrete floor serving as a bottom. A brick flue was not considered necessary—since only the drop in pressure through the orifice was

measured and all other rubbing surfaces would have but little effect.

A brick wall was built about nine feet from the fan inlet in the flue. A greater distance than this was desirable but more space was not available. The orifice in the center of the diaphragm was made square. The brick were laid in cement mortar, and all cracks and openings between the diaphragm and the flue were made air-tight.

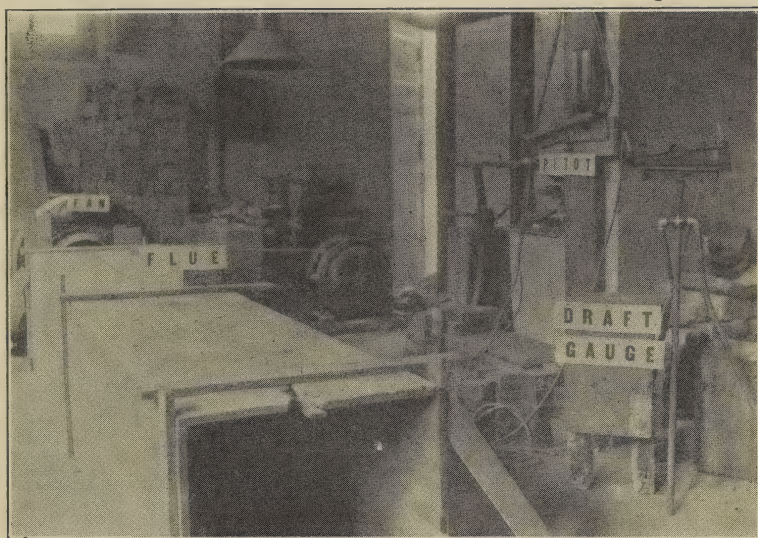


FIG. 1.

Orifices of two sizes were tried. The area of the first was equal to about 25 per cent. of the area of the vertical section of the flue. With a velocity of ten feet per second through the flue, the draft gage registered a drop of 0.42 inch W. G. through this orifice. This was considered excessive since the draft would undoubtedly be seriously affected by much added resistance. An orifice having an area of about 50 per cent. of the flue was then constructed. With this orifice, the drop under the same velocity was but 0.13 inch W. G. and at the lowest velocities was about 0.015 inch W. G. An orifice of this size was therefore adopted. The area of the orifice (26" \times 26") was a little larger than one-half (55 per

cent.) the area of the flue. A sketch of the part of the flue containing the diaphragm is shown in Fig. 2.

In order to make the conditions more comparable to those actually found in flues leading from kiln to stack, the end of the flue was partly closed. The obstruction served as the resistance offered to the flow of the gases by the furnaces and kiln, and was made equal to about 0.2 inch W. G. under maximum velocity conditions. It has been found that, for ordinary round kilns, the draft gage reaches a maximum of about 0.2 inch W. G. The

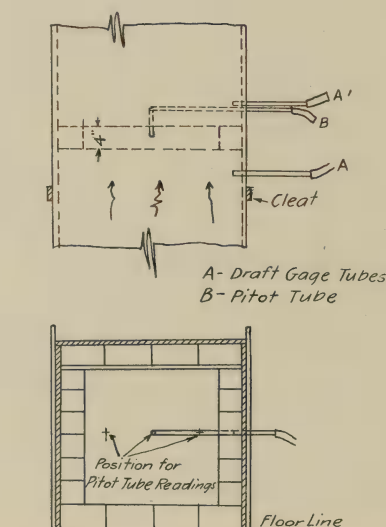


FIG. 2.—Portion of flue showing diaphragm and positions of tubes.

draft gage tube "A" (Fig. 2) between the diaphragm and the end of the flue would therefore register a pressure of 0.2 inch plus the resistance from the end of the flue to the tube, while the draft gage tube "A" beyond the diaphragm would read this resistance plus the resistance offered by the diaphragm. These gage tubes were placed about three inches from the diaphragm on each side and entered the flue through holes in the center of one side. They projected about one inch into the flue but this distance is not important since the gage reading was not affected by any change.

Measurements.

A Pitot tube was used to measure the velocity of the gas through the orifice for every reading taken on the draft gage. The Pitot tube was practical in this case for we had a straight flow of gas and the velocity through the orifice—400 to 1000 feet per minute—was high enough to assure accuracy. The Pitot tube was inserted just behind the diaphragm (Fig. 2) and through the same opening used for the draft gage tube—the bent end of the Pitot tube reaching just to the center of the wall. The Pitot tube therefore gave the pressures existing in the orifice. Three readings were taken across the orifice, as marked in Fig. 2—the average of these being taken as the average pressure in the orifice.

An inclined manometer, which could be so adjusted that from two to forty inches of slant along the manometer was equivalent to one inch of vertical reading, was used. The forty-inch slope of the manometer assured an accurate reading with low velocities. In converting the manometer readings to inches of water gage, they were multiplied by the specific gravity of the oil used (0.837).

Since one part of the Pitot tube gives total pressure and the other static pressure, the difference being the velocity pressure, if each tube is connected to the ends of the manometer tube, the differential reading will be the velocity pressure. To illustrate, suppose a reading is 3.82 and the manometer is set at a slope of 20 (that is, 20 inches on the manometer being equivalent to one-inch vertical reading). Then $3.82 \div 20 = 0.191''$ vertical reading. Multiplying by 0.837, the specific gravity of the oil, $0.191 \times 0.837 = 0.16''$ W. G. = the velocity pressure. The velocity of the gas is then determined by means of the formula—

$$V = K\sqrt{p},$$

where V = velocity in feet per minute,

p = velocity pressure in inches W. G.,

and K = velocity constant.

The velocity constant K changes with the temperature. At 70° F. it is 4006. A table giving these constants is included later. The photograph (Fig. 1) shows the arrangement of the entire apparatus. The inclined manometer is shown directly above the word "Pitot."

Before making any tests, readings of the Pitot tube were checked against the tubes used with the draft gage for static pressure. The manometer was also checked against the draft gage. Each tube was inserted at the same time, the fan operated, and the following results were obtained:

Draft gage tube.....	{	On draft gage....	0.587 inch W. G.
		On manometer...	0.591 inch W. G.
Pitot tube (static pressure)....	{	On draft gage....	0.579 inch W. G.
		On manometer...	0.582 inch W. G.

The readings of the Pitot tube and draft gage tubes varied less than 0.01, differing but 0.008, and the manometer and draft gage differed but 0.004. This was quite satisfactory and gave us more confidence in the readings of the Pitot tube.

The Tests.

In making the tests, the velocity through the flue was varied—200 feet per minute being the minimum. By partly closing the outlet of the fan, any desired velocity could be obtained.

The results secured with the 35" by 35" flue and 26" by 26" orifice are tabulated as follows:

TABLE I.

Static pressure before diaphragm (Tube A' in Fig. 2).	Differential reading (draft gage).	Manometer.	Slope.	Velocity through orifice in feet per minute.	Remarks.
0.02	0.017	0.4	40	370	Temperature 80° F.
0.048	0.04	1.00	40	587	Specific gravity of oil 0.837
0.065	0.052	1.30	40	668	Formula to figure velocity—
0.085	0.07	1.93	40	815	$V = K\sqrt{p}$.
0.12	0.10	2.45	40	917	K at 80° F. = 4044
0.13	0.107	2.57	40	938	Unrestricted outlet.
0.155	0.116	2.78	40	977	
0.17	0.12	2.90	40	995	
0.19	0.125	3.07	40	1030	

The size of the flue was next reduced to 23½" by 22½" (3.67 square feet). The area of the orifice was made 55 per cent. of that of the flue or 2.02 sq. ft. (17" × 17").

The results for a flue of this size are tabulated as follows:

TABLE 2.

Static pressure before diaphragm.	Differential reading.	Manometer.	Slope.	Velocity through orifice F. P. M.	Remarks.
0.02	0.015	0.18	20	351	Temperature 82° F.
0.027	0.022	0.29	20	446	K at 82° = 4050
0.034	0.028	0.33	20	476	
0.045	0.035	0.40	20	523	
0.057	0.048	0.55	20	614	
0.06	0.05	0.58	20	630	
0.09	0.062	0.88	20	776	
0.13	0.08	1.23	20	918	
0.15	0.11	1.30	20	945	
0.19	0.123	1.55	20	1030	

If the results secured by the use of the two orifices are compared, it will be found that they check very closely. For instance, for 370 feet per minute in the larger flue, a drop of 0.017 inch through the orifice was noted, while for 351 feet per minute in the smaller flue, we noted a drop of 0.015 inch. Again, with 1030 feet per minute in both flues, we noted 0.123 inch drop in one case and 0.125 inch in the other. This appears to indicate that if the ratio of the areas of orifices and flues are kept constant, the same drop in pressure through the orifice occurs with the same velocity—the size of the flue being unimportant.

The accuracy of the readings was tested by the use of the relation, "pressure or resistance varies as the square of the velocity." The average of the two tests was taken from the following condensed results (Table 3) giving only the drop in pressure through the orifice for the corresponding velocity. The higher velocities, 1100 to 1600 feet per minute, which the fan could not produce, were calculated from the pressure-velocity relation (Table 4). Under "ratio" is given the ratio of the first reading of pressure to every other pressure. The second ratio column gives the same for the velocities. Any pressure ratio should, therefore, be theoretically equal to the square of the corresponding velocity ratio.

TABLE 3.

Large flue.		Small flue.	
Pressure drop.	Velocity.	Pressure drop.	Velocity.
0.017	370	0.015	351
0.04	587	0.022	446
0.052	668	0.028	476
0.07	815	0.035	523
0.10	917	0.048	614
0.107	938	0.05	630
0.116	977	0.062	776
0.12	995	0.08	918
0.125	1030	0.11	945
0.150	1100	0.123	1030
0.178	1200	0.147	1100
0.210	1300	0.176	1200
0.243	1400	0.206	1300
0.279	1500	0.238	1400
0.318	1600	0.273	1500
...	..	0.312	1600

TABLE 4.—AVERAGE FOR TEMPERATURE OF 80° F.

Pressure drop.	Ratio.	Velocity through orifice.	Ratio.	Velocity through flue.
0.016	...	360	..	198
0.028	1.75	482	1.34	266
0.044	2.75	600	1.66	330
0.051	3.19	650	1.81	357
0.066	4.12	796	2.21	407
0.09	5.62	918	2.55	473
0.1107	6.92	952	2.64	523
0.115	7.19	970	2.69	533
0.124	7.75	1030	2.86	555
0.1485	9.29	1100	3.06	605
0.177	11.07	1200	3.34	660
0.208	13.0	1300	3.62	715
0.2405	15.03	1400	3.89	770
0.276	17.25	1500	4.17	825
0.315	19.68	1600	4.45	880

These ratios were plotted against each other and checked by drawing the theoretical pressure-velocity curves on the same chart (Fig. 3). With but two exceptions (the pressure drops of 0.066 inch and 0.09 inch) all points fall upon the curve. This appears to indicate that the drop in pressure through an orifice

is an accurate indication of the velocity of the air passing through a flue. The results were put in more convenient form by means of curves so that the velocities could be determined directly from the differential reading, providing the temperature is known

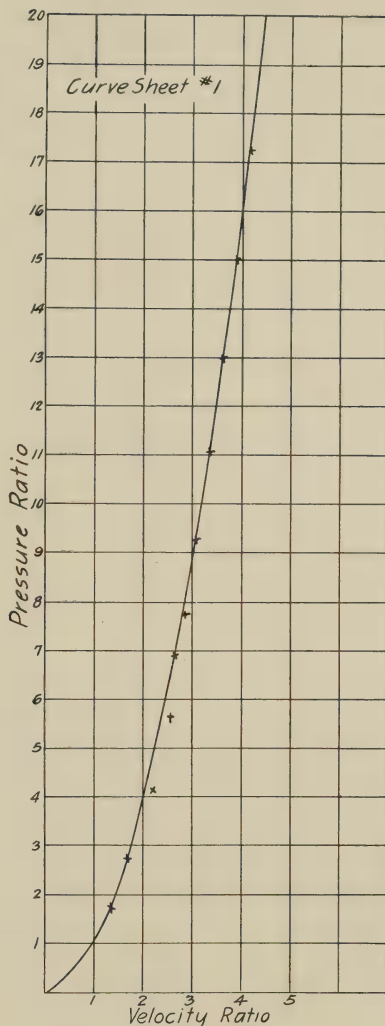


FIG. 3.

and the same ratio of orifice and flue, as used in this investigation, is employed.

The temperature of the gas is an important factor in the pressure developed at a certain velocity. It would appear that, as the temperature increases and the sp. gr. of the gas decreases, the pressure developed at a constant velocity becomes lower. Since the results (Table 4) were taken at a temperature of about 80° F., they cannot be applied to conditions in a flue, the temperature of which may be 1500° F. Results for the different temperatures must therefore be obtained.

A very simple method of converting the pressures from one temperature to that at another temperature was obtained by the use of the following "Table of Constants" (Table 5)¹ giving the velocity constants already mentioned for any temperature.

In Table 5, K represents the velocities of dry air, in feet per minute, required to sustain a column of water one inch in height. This was obtained by using the formula

$$k = \sqrt{\frac{2g \times \text{weight of 1 cu. ft. of water at 62° F.}}{12 \times \text{weight of 1 cu. ft. of air at temp. stated.}}}$$

Small k in the formula is the velocity in feet per second and is multiplied by 60 to secure the values for K given in the table. g = acceleration due to gravity = 32.16.

The ratios given in the table are those between the fan speeds necessary for the various temperatures listed and 70° F. to produce the same water gage indication.

The table is used as follows: To change any pressure, say at 80° F. to that at 200° F. under the same velocity, divide the pressure at 80° F. by the square of the ratio of the velocity constant at 200° F. to the velocity constant at 80° F. For example, suppose we take the differential reading obtained for a velocity of 1600 feet per minute through the orifice or 880 feet per minute through the flue, which is 0.315 inch W. G. at 80° F., the temperature of the experiment. The ratio of the velocity constants at 200° F. and 80° F. would be $\frac{4470}{4044} \cdot \left(\frac{4470}{4044}\right)^2 = 1.22 =$ the fac-

¹ This table was obtained from Mr. L. E. Eisensmith of the American Blower Co.

tor by which all pressures at 80° F. must be divided in order to obtain the pressure at 200° F. $0.315 \div 1.22 = 0.258$. The pressure at 880 feet per minute at a temperature of 200° F. would therefore be 0.258 inch W. G.

TABLE 5.—CONSTANTS.

Figured for dry air at sea level.
Barometer 29.92 inches mercury.

Temperature.	K.	Ratio.	Temperature.	K.	Ratio.
40° F.	3567	0.890	480° F.	5332	1.331
30	3609	0.901	500	5389	1.345
20	3651	0.911	520	5445	1.359
10	3692	0.921	540	5500	1.373
0	3733	0.932	560	5555	1.387
10	3773	0.942	580	5609	1.400
20	3813	0.952	600	5663	1.413
30	3852	0.961	620	5716	1.426
40	3891	0.971	640	5769	1.439
50	3930	0.981	660	5821	1.452
60	3968	0.990	680	5873	1.465
70	4006	1.000	700	5925	1.478
80	4044	1.009	720	5976	1.491
90	4081	1.018	740	6027	1.504
100	4118	1.028	760	6077	1.517
110	4155	1.037	780	6127	1.530
120	4191	1.046	800	6177	1.542
130	4227	1.055	820	6226	1.554
140	4263	1.064	840	6275	1.566
150	4298	1.073	860	6323	1.578
160	4333	1.082	880	6371	1.590
170	4368	1.090	900	6418	1.602
180	4402	1.098	920	6465	1.614
190	4436	1.106	940	6512	1.626
200	4470	1.114	960	6558	1.638
220	4537	1.132	980	6604	1.649
240	4603	1.149	1000	6650	1.660
260	4668	1.165	1020	6695	1.671
280	4732	1.181	1040	6740	1.682
300	4796	1.197	1060	6785	1.693
320	4851	1.213	1080	6829	1.704
340	4921	1.228	1100	6873	1.715
360	4982	1.243	1120	6918	1.726
380	5042	1.258	1140	6962	1.737
400	5101	1.273	1160	7005	1.748
420	5159	1.288	1180	7048	1.759
440	5217	1.303	1200	7090	1.770
460	5275	1.317

In this way the pressures at 80° F. were converted into those at temperatures up to 1500° F. The results for each temperature were plotted as shown in Fig. 4. In plotting, the two velocities corresponding to the two points which were off the pressure-velocity curve were corrected in order to make the final curves

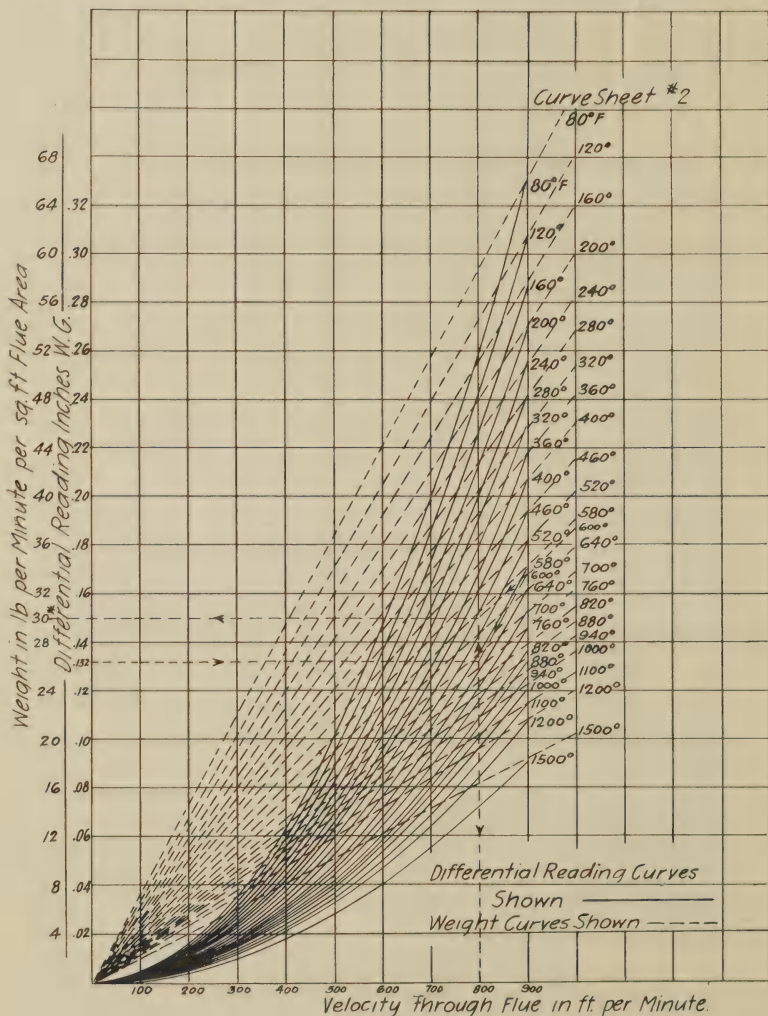


FIG. 4.

more accurate. From these curves, the velocity through the flue at any temperature can be secured from the differential draft gage reading. However, even the velocities may become misleading, since the same velocity at different temperatures does not mean the same weight of gases, and the weight of the gases after all is what we must have in order to determine the rate of combustion we are getting in the fire boxes. A set of velocity weight curves for the different temperatures was therefore drawn directly over the differential draft gage reading curves, and from this double set of curves the weight of the gas may be determined directly from the differential reading on the draft gage. This weight is expressed in pounds per minute per square foot of flue area—since this forms a basis from which the actual weight of gas can be figured for any flue. The weights are based on dry air—since the data in the "Table of Constants" was figured on the same basis. A source of error is introduced here since the weight of the air varies as the relative changes in humidity. However, the most useful part of these curves is from about 300° F. and higher. The relative humidity must become very low as the temperature increases beyond this point and the error should not be great enough to make the results unreliable.

An illustration of the use of the curves is indicated in Fig. 4. Assume a reading of 0.132 inch W. G. at a temperature of 600° F. in the flue. Approximating 600° F. on the solid line curves, we come down until we strike 0.132 on the differential reading scale. If we wish to determine the velocity, we drop to the abscissa and find it to be 800 feet per minute. To get the weight we proceed vertically in the direction of the arrow until we strike the approximate 600° F. curve on the broken line set of weight curves. We then go to the left to the weight scale along the ordinate and find it to be 30.

Conclusions.

Lack of time prevented any additional work. Since the differential readings at the higher temperatures are not very large, it would be interesting to run similar tests with a somewhat smaller orifice in order to determine the relation between the size of the orifice and the differential readings. It is very doubtful whether the orifice should be made smaller since the size used

produced a static pressure drop of somewhat over 0.1 inch W. G. The addition of 0.1 inch W. G. of static pressure to a stack would very likely push it to its limit in order to maintain sufficient velocity pressure to produce the desired draft movement.

It is interesting to note that, with induced draft, the static pressure gives a higher reading than the total pressure. The relation—"total pressure minus static pressure equals velocity pressure"—still holds, however, since in induced draft they are both negative and by subtracting the static from the total pressure we get a positive velocity pressure which is as it should be. For example, if we have a total pressure of 0.4 inch W. G. and a static pressure of 0.6 inch W. G.,

$$\text{then } T. P. - S. P. = V. P.$$

$$-0.4 - (-0.6) = +0.2.$$

With this, a possible method of using the draft gage to measure velocities and weights in a flue has been found. However, the work is merely experimental and should be tried out under actual conditions in order to determine its practicability. It shows possibilities and might, with some alterations, be of value in the firing of kilns. Conditions vary at every plant, but there seems to be no reason why any one plant could not prepare a set of readings by this method for use in noting whether or not the burn is progressing satisfactorily.

DISCUSSION.

MR. DAVENPORT: I would like to ask Mr. Harrop whether the minimum static pressure observed in these tests was comparable with the minimum observed in ordinary kiln firing. Although the data presented is interesting from the theoretical standpoint, it has been my experience that the very low draft pressures involved in periodic kiln firing render it exceedingly difficult to secure reliable readings. Mechanical engineers have about given up the problem of trying to read pressure differences amounting to only 0.04" to 0.05" of water.

MR. HARROP: Our method of measuring the pressure involved the use of a manometer similar to that used by the American

Blower Company. This manometer may be set at a very low angle and is very sensitive. I realize that it is very difficult to secure an accurate reading in this way, but to my knowledge this manometer is the most delicate instrument available for use in measuring the velocity pressure by the Pitot tube method. In regard to the pressures employed, the static pressure resulting from the resistance through a kiln at the beginning of a burn was taken as 0.02" and was determined by an actual kiln reading. This static pressure of 0.02" resulted from the resistance of the kiln to the flow of gases. In other words, that static pressure would have shown up on the kiln side of the diaphragm. As the burn continued the static pressure increased to about 0.21" at the highest temperature.

MR. DAVENPORT: I would like to add that this problem of the determination of the amount of air or gas moving through kilns is an important one, but I would also like to emphasize the fact that it is a complex one and one which has for some time baffled the best efforts of mechanical engineers. The Thomas Electric meter seems to offer one practically reliable method of determining the flow of gases at very low velocity pressures; but in my own experience with Pitot tubes I have found, inasmuch as the variation may be as much as 50 per cent. plus or minus, that an endeavor to reduce the results to absolute values below about 0.05" is fruitless. I believe, however, that if work of this kind were undertaken by ceramic engineers and an active demand were created for some means of measuring very low draft pressures, that some good would come of it; but at present the Pitot tube and slant gage are conceded by most authorities to be exceedingly unsatisfactory for the measurement of low velocities.

COMMUNICATED DISCUSSIONS.

ELLIS LOVEJOY: Mr. Fritz has given us a very creditable piece of work and it is to be hoped that it will lead to some improvement in the important burning operations.

I have had no respect for a draft gage for some time and the majority of clay workers are also lacking in respect—if I may judge from the number of gages I have seen entirely out of com-

mission, or running their course of uselessness without any attention. Where records are kept, the firemen have settled down to filling in the spaces in a prefatory manner without even reading the gages and the data slips are added to the dusty pile in the corner of the kiln house.

A draft gage attached to a chambered continuous kiln compartment will show several tenths minus pressure in the early stages of the compartment's operation. As the fires approach the compartment in question, the pressure will drop back to zero and often go beyond, indicating no draft, in fact a back pressure, yet the operation of the kiln moves along in spite of the readings of the draft gage. The behavior is easily explained and the explanation condemns the draft gage.

A differential gage will, as Mr. Fritz has shown, give us correct draft readings which may be reduced to velocity and to volume of gas moved. The attachment of such a gage to a kiln is a problem in itself.

Consider the chambered continuous kiln for example. The natural location for the gage would be in the long flue connecting the kiln to the stack or fan, but in the modern kiln there are two distinct operations carried on by the fan draft; namely, burning and water-smoking, each under damper control. Draft gage readings beyond these dampers would be of no value and there is no room between the dampers and the kiln as a rule. It would be impracticable to make the connections on opposite sides of the chamber division walls because of the wide difference in temperature.

Down-draft kilns may have wall stacks, outside stacks in close proximity to the kiln, or distant stack or fan. In the first two instances the differential gage could only be attached to the stack with such adjustments as may be necessary for the difference in altitude. The stack, and this is also true of any flue, must be large enough to accommodate a suitable diaphragm having an opening of requisite size for the kiln operation and there will be an essential difference in temperature for which correction must be made.

Besides the difference in temperature on opposite sides of the diaphragm, we must take into consideration the constantly ad-

vancing temperature in the kiln flue and stack, and we must also consider that the stack and flue temperatures, will vary widely at any given stage in successive burns, and it is not safe to assume that, if on the sixth day of one burn we have 0.3 inch water gage draft, this will be the proper draft for the sixth day of any other burn.

The draft gage to be useful to the clay workers is not to tell them what has been done but to direct the work in the future. Its real purpose is to enable the manager to put in the kiln house a diagram showing the burner just what the draft gage should read at every stage in the process to the end of the burn.

How far the draft gage may become useful in kiln operations remains to be seen, but it will, in kiln tests under competent handling, determine proper kiln pressures for various wares in several types of kilns and thus give us the necessary data for better kiln design and construction.

Mr. Fritz states that for ordinary round kilns the draft reaches a maximum of about 0.2 inch water gage.

I have been seeking this data for some time and if he has accurate records along this line I should very much like to have them. Down draft kilns vary widely in the construction of the floor flue system and there is a greater variation in the kiln setting.

A gas burning kiln with a simple floor system set with drain tile or other hollow ware is a very different matter from a closely set face brick kiln with a complicated floor flue system, burned with coal fired in grate bar furnace.

It seems to me that 0.2 inch water gage is too low for a maximum resistance in down draft kilns, and I am inclined not to accept it without further proofs of actual tests under maximum resistance conditions.

C. B. HARROP: Regarding the statement in the impromptu discussion offered by Mr. Davenport, relative to the impracticability of Pitot tube readings under low pressure conditions, attention should be called to two points: First, as the diaphragm orifice (where the Pitot tube was placed) was approximately 50 per cent. of the area of the flue, the velocity through the orifice

was approximately double that through the flue. This gave at all times sufficient velocities to be satisfactorily read with the Pitot tube. Second (as shown in Fig. 3), the relation between velocities determined by the Pitot tube and resistance or pressure drop results in practically a perfect " R varies as V^2 " curve, which in itself proves that the Pitot tube readings were amply accurate for the work.

THE CLAYS OF FLORIDA.

By E. H. SELLARDS.

The clays of Florida that are being utilized include those from which building brick and tile are made, the white-burning ball clays or plastic kaolins, and fuller's earth. The production of building brick during 1916 amounted to 31,129 million, the value of which, including a small amount of tile and fire-proofing brick, was \$226,362. The production of plastic kaolin is limited at the present time to the output of three plants under the management of two companies. During 1916 five plants were engaged in mining fullers' earth, the production from these five plants being about 90 per cent. of the total production of this material in the United States.

In their geologic relation the clays of Florida all lie above the Oligocene limestones since beneath these formations are Eocene limestones which, at least in the peninsular section of the State, extend uninterruptedly to a great depth.

The fuller's earth clays lie within the Alum Bluff formation which, according to the vertebrate fauna obtained within recent years, is Miocene. The clays used in brick making vary in age probably from the Miocene to the Pleistocene or Recent. The geographic distribution of the clays likewise is irregular, although all that are being utilized are found in the northern part of the State—within 200 miles or less of the north line.

The Florida Common Clays.

No clays suitable for making vitrified brick have been located within the State. In 1915 a series of tests of 25 samples of Florida clays was made by the Bureau of Standards laboratory at Pittsburgh. The clay samples for these tests were collected by the Florida Geological Survey. The 25 samples tested represented clays from 21 counties in Florida. Each sample approximated 250 pounds in weight and was representative, as nearly as could

be judged, of the clay of the locality from which it was taken. These tests were not successful in locating any clays that would serve in the manufacture of vitrified brick. Although previously published in the reports of the Florida Geological Survey, the results from a few of these 25 tests on the common clays of Florida may be here included for convenience of reference.

Sample No. 1, Jackson County.—The clay works with some difficulty in the stiff-mud condition; water of plasticity in per cent. of dry weight, 40.80 per cent.; warped and cracked during the drying treatment; linear drying shrinkage, in terms of wet length, 9.95 per cent.; linear burning shrinkage in terms of dry length, at 850° C., 0.77 per cent.; at 1010° C., 4.59 per cent.; at 1130° C., 6.60 per cent.; at 1250° C., 7.55 per cent.; color after burning, light red at lower temperatures, changing to dark red at higher; per cent. porosity, at 850° C., 36.75 per cent.; at 950° C., 40.55 per cent.; at 980° C., 34.30 per cent.; at 1010° C., 30.30 per cent.; at 1040° C., 24.20 per cent.; at 1070° C., 24.00 per cent.; at 1100° C., 26.10 per cent.; at 1130° C., 25.15 per cent.; at 1160° C., 23.65 per cent.; at 1190° C., 23.60 per cent.; at 1220° C., 23.85 per cent.; at 1250° C., 20.70 per cent. A somewhat plastic and sticky clay of high drying and burning shrinkage. The clay retains a porous structure at 1250° C., and cannot be used in the manufacture of vitrified ware burned in commercial kilns. The clay may be used in the manufacture of common and building brick.

Sample No. 2, Washington County.—The clay possesses good working plasticity and molding behavior; water of plasticity, 36.0 per cent.; a few cracks developed by drying; linear drying shrinkage, 9.42 per cent.; linear burning shrinkage, at 850° C., 0.55 per cent.; at 1010° C., 1.57 per cent.; at 1130° C., 7.75 per cent.; at 1250° C., 8.10 per cent. A good light buff color is developed by burning; per cent. porosity, at 850° C., 36.80 per cent.; at 950° C., 35.30 per cent.; at 980° C., 34.75 per cent.; at 1010° C., 34.50 per cent.; at 1040° C., 30.75 per cent.; at 1070° C., 25.70 per cent.; at 1100° C., 22.45 per cent.; at 1130° C., 19.70 per cent.; at 1160° C., 17.95 per cent.; at 1190° C., 15.70 per cent.; at 1220° C., 14.60 per cent.; at 1250° C., 12.55 per cent. A buff burning clay of good plasticity and a relatively high drying shrinkage.

May be used in the manufacture of buff colored face brick, although care must be exercised in drying. The clay must be burned above 1250°C . in order to attain low porosity.

Sample No. 3, Santa Rosa County.—The clay has good working plasticity and molding properties; water of plasticity, 28.90 per cent.; no drying difficulties; linear drying shrinkage, 6 per cent.; linear burning shrinkage, at 850°C ., 0.64 per cent.; at 1010°C ., 0.21 per cent.; at 1130°C ., 1.44 per cent.; at 1250°C ., 1.17 per cent.; burns to salmon color, changing to buff at higher temperature; per cent. porosity, at 850°C ., 35.30 per cent.; at 950°C ., 35.80 per cent.; at 980°C ., 36.20 per cent.; at 1010°C ., 34.86 per cent.; at 1040°C ., 33.60 per cent.; at 1070°C ., 32.15 per cent.; at 1100°C ., 31.10 per cent.; at 1130°C ., 29.55 per cent.; at 1160°C ., 29.05 per cent.; at 1190°C ., 28.80 per cent.; at 1220°C ., 28.05 per cent.; at 1250°C ., 27.30 per cent. A clay possessing good working and drying qualities but which cannot be vitrified at the burning temperatures of commercial kilns. Test pieces burned to 1250°C . are easily cut by a knife. This clay is of value only in the manufacture of porous common building brick, etc.

Sample No. 4, Escambia County.—Appears to have good working behavior and plasticity; water of plasticity, 21.95 per cent.; drying behavior satisfactory; linear drying shrinkage, 5.75 per cent.; linear burning shrinkage, at 850°C ., 1.28 per cent.; at 1010°C ., 0.05 per cent.; at 1130°C ., 0.26 per cent.; at 1250°C ., 1.16 per cent.; color after burning, light to dark red; per cent. porosity, at 850°C ., 28.65 per cent.; at 950°C ., 29.30 per cent.; at 980°C ., 28.20 per cent.; at 1010°C ., 27.90 per cent.; at 1040°C ., 27.75 per cent.; at 1070°C ., 25.85 per cent.; at 1100°C ., 26.95 per cent.; at 1130°C ., 25.70 per cent.; at 1160°C ., 27.95 per cent.; at 1190°C ., 26.80 per cent.; at 1220°C ., 19.90 per cent.; at 1250°C ., 20.20 per cent. A clay possessing good working and drying behavior, but one which retains a porous structure at temperatures as high as 1250°C . The clay is suitable for common and face brick, etc., but not for paving brick or other vitrified ware.

Sample No. 5, Walton County.—Plasticity and working properties good; water of plasticity, 28.30 per cent.; drying behavior

satisfactory; linear drying shrinkage, 6.75 per cent.; linear burning shrinkage, at 850° C., 0.34 per cent.; at 1010° C., 0.35 per cent.; at 1130° C., 2.17 per cent.; at 1250° C., 2.25 per cent.; color after burning, salmon to light red; per cent. porosity, at 850° C., 33.60 per cent.; at 950° C., 33.20 per cent.; at 980° C., 35.40 per cent.; at 1010° C., 34.35 per cent.; at 1040° C., 32.80 per cent.; at 1070° C., 30.50 per cent.; at 1100° C., 29.85 per cent.; at 1130° C., 28.60 per cent.; at 1160° C., 27.55 per cent.; at 1190° C., 27.80 per cent.; at 1220° C., 27.10 per cent.; at 1250° C., 26.00 per cent. A red burning clay having good working and drying behavior, but retaining a porous structure. Test pieces burned to 1250° C. are easily scratched by a knife. This clay is suitable for the manufacture of porous common and building brick. Not practical to vitrify in commercial kilns.

Sample No. 11, Duval County.—Fairly plastic, fairly good working qualities; water of plasticity, 27.4 per cent.; dries satisfactorily; linear drying shrinkage, 9.6 per cent.; linear burning shrinkage, at 990° C., 0.05 per cent.; at 1110° C., 0.82 per cent.; at 1230° C., 2.34 per cent.; at 1320° C., 3.97 per cent.; red burning; per cent. porosity, at 850° C., 28.1 per cent.; at 950° C., 26.8 per cent.; at 980° C., 25.7 per cent.; at 1010° C., 25.8 per cent.; at 1040° C., 24.8 per cent.; at 1070° C., 24.6 per cent.; at 1100° C., 22.5 per cent.; at 1130° C., 22.5 per cent.; at 1160° C., 20.4 per cent.; at 1190° C., 16.6 per cent.; at 1220° C., 11.5 per cent.; at 1250° C., 7.5 per cent. A sandy surface clay of fair working and drying behavior. A decrease in porosity is noted with increase in temperature, although it is doubtful whether a vitrified product may be manufactured from this material, owing to the relatively high temperatures necessary.

Sample No. 12, Clay County.—Very plastic, and possesses fair working qualities; water of plasticity, 34.4 per cent.; excessive drying shrinkage; linear drying shrinkage, 12.22 per cent.; linear burning shrinkage, at 990° C., 1.45 per cent.; at 1110° C., 3.48 per cent.; at 1230° C., 4.87 per cent.; red burning; per cent. porosity, at 850° C., 24.4 per cent.; at 950° C., 22.7 per cent.; at 980° C., 19.6 per cent.; at 1010° C., 18.7 per cent.; at 1040° C., 18.7 per cent.; at 1070° C., 17.4 per cent.; at 1100° C., 17.3 per cent.; at 1130° C., 16.8 per cent.; at 1160° C., 16.9 per cent., at 1190° C.,

16.0 per cent.; at 1220° C., 14.4 per cent.; at 1250° C., 13.8 per cent. A plastic red burning clay having a high drying shrinkage. Care must be exercised in drying heavy pieces. This clay has a relatively low porosity at commercial kiln temperatures and attains a fairly dense structure.

Sample No. 21, Jefferson County.—Medium plastic with fair working properties; water of plasticity, 32.6 per cent.; no drying difficulties; linear drying shrinkage, 9.77 per cent.; linear burning shrinkage, at 990° C., 0.22 per cent.; at 1110° C., 1.09 per cent.; at 1230° C., 0.55 per cent.; at 1320° C., 0.49 per cent.; buff burning; per cent. porosity, at 990° C., 35.6 per cent.; at 1020° C., 34.0 per cent.; at 1050° C., 33.2 per cent.; at 1080° C., 33.4 per cent.; at 1110° C., 33.8 per cent.; at 1140° C., 33.6 per cent.; at 1170° C., 33.6 per cent.; at 1200° C., 33.7 per cent.; at 1230° C., 32.8 per cent.; at 1260° C., 34.4 per cent.; at 1290° C., 33.7 per cent.; at 1320° C., 33.5 per cent. A sandy buff burning clay which retains an open porous structure at temperatures up to 1320° C. May have some use in the manufacture of soft porous common building brick.

Sample No. 22, Polk County.—Medium plastic with fair working properties; water of plasticity, 24.9 per cent.; no drying difficulties; linear drying shrinkage, 6.28 per cent.; linear burning shrinkage, at 950° C., 0.37 per cent.; at 1100° C., 0.47 per cent.; at 1220° C., 0.08 per cent.; at 1310° C., 0.24 per cent.; burns red; per cent. porosity, at 950° C., 35.6 per cent.; at 1010° C., 35.8 per cent.; at 1040° C., 35.6 per cent.; at 1070° C., 36.0 per cent.; at 1100° C., 34.8 per cent.; at 1130° C., 33.8 per cent.; at 1160° C., 33.8 per cent.; at 1190° C., 33.7 per cent.; at 1220° C., 33.6 per cent.; at 1250° C., 33.7 per cent.; at 1280° C., 33.4 per cent.; at 1310° C., 33.6 per cent. A sandy red burning material which retains an open porous structure at temperatures up to 1320° C. May have some use in the manufacture of soft porous common building brick.

The Florida Plastic Kaolins.

Occurrence.—The plastic kaolins of Florida present problems of exceptional interest. The formation which holds the clays is

probably co-extensive or nearly so with the physiographic type known as the Lake Region of Florida. This belt of country extends in the peninsula of Florida from Clay County on the north to near the middle of DeSoto County on the south, a distance of about 150 miles. In width the belt varies from 10 to 30 or 40 miles. Small lakes are numerous. Their basins, as a rule, are circular in outline and relatively deep with steep sides. The uplands are sandy and well drained. A similar type of topography, underlaid probably by the same formation, is found in several counties in west Florida between the Suwanee and Choctaw-hatchee rivers.

The clay in this formation is intimately associated with coarse sand from which it is removed by washing. Mica is also present and is removed by screening. The sand in this formation is usually coarse and in places affords the sharpest and best building sand found in Florida.

The place of the clay-bearing formation in the geologic time scale is difficult to determine owing to the complete absence of fossils. It overlies the Oligocene limestones. There is also some reason for believing that it lies at a stratigraphic level higher than the fuller's earth beds and hence is not older than the Miocene. However, inasmuch as no one of the later fossiliferous formations is found overlying this formation, it has not been possible to fix its age more definitely.

The two localities at which this clay is being worked are Edgar in Putnam County and Okahumpka in Lake County. At Edgar, 4 to 10 feet of loose sand lies above the kaolin-bearing sand. This top sand is coarse—containing silicious pebbles up to one-third of an inch across. The large pebbles are flattened and all are rounded. The kaolin-bearing sands beneath are gray in color, although the weathered surface is sometimes slightly iron-stained. They are said to have a total thickness of 30 feet or more and are underlaid by a sticky, blue clay. It is reported that beneath the blue clay a fuller's earth occurs, and that this in turn passes at a depth of about 70 feet into a scarcely indurated shell stratum. A well put down by the Edgar Plastic Kaolin Company is reported to have passed through coarse superficial sand, 10 feet; kaolin-bearing sands, 30 or more feet; sticky, blue clay with fuller's

earth beneath, about 40 feet; scarcely indurated shell stratum, 20 feet. The well terminated on a hard limestone at the depth of 90 feet, probably the Chattahoochee limestone, which is Upper Oligocene in age, or possibly the Eocene limestones which lie next beneath—the Chattahoochee formation being usually wanting along the eastern slope of the peninsula.

The kaolin in Lake County occurs under conditions similar to those found in Putnam County. The superficial sands here, as at the Edgar mines, are coarse and contain white, silicious pebbles. The kaolin-bearing sands are gray in color except where stained red with iron. A small amount of mica, found in the kaolin sands, is screened out in the process of washing.

The sand-clay mixture of this formation is often well adapted to road construction, and is frequently so used, especially when somewhat colored by iron-staining as it often is near the surface.

The Florida kaolin-bearing formation is plainly sedimentary in origin and represents, as indicated by the rather coarse sand, a relatively near-shore accumulation of material. The association of the finely divided clay with the coarse quartz sand and the mica is one of the problems of this formation.

Mining.—In mining the Florida kaolin the overburden, which consists of a few feet of sand or iron-stained sand and clay, is removed—usually by the hydraulic process. The clay itself is lifted chiefly by suction pumps which are carried on a floating dredge. The pits are first of all opened to the water table level, which lies at a moderate although varying depth, depending upon the topography. The dredges are then floated on the water that accumulates in the pit. The dredge itself carries a relay station. On some of the dredges this relay pumping station, corresponding to the sump-hole of ordinary hydraulicing, is itself submerged. The pump removing the clay from the sump-hole has a capacity slightly greater than the pump which brings the clay to the sump-hole. Thus, notwithstanding the fact that the process goes on just below the surface of the water, no part of the clay is lost at the relay station because all that goes into the bin is removed at once—the suction of the pump preventing the escape of the floating particles of clay.

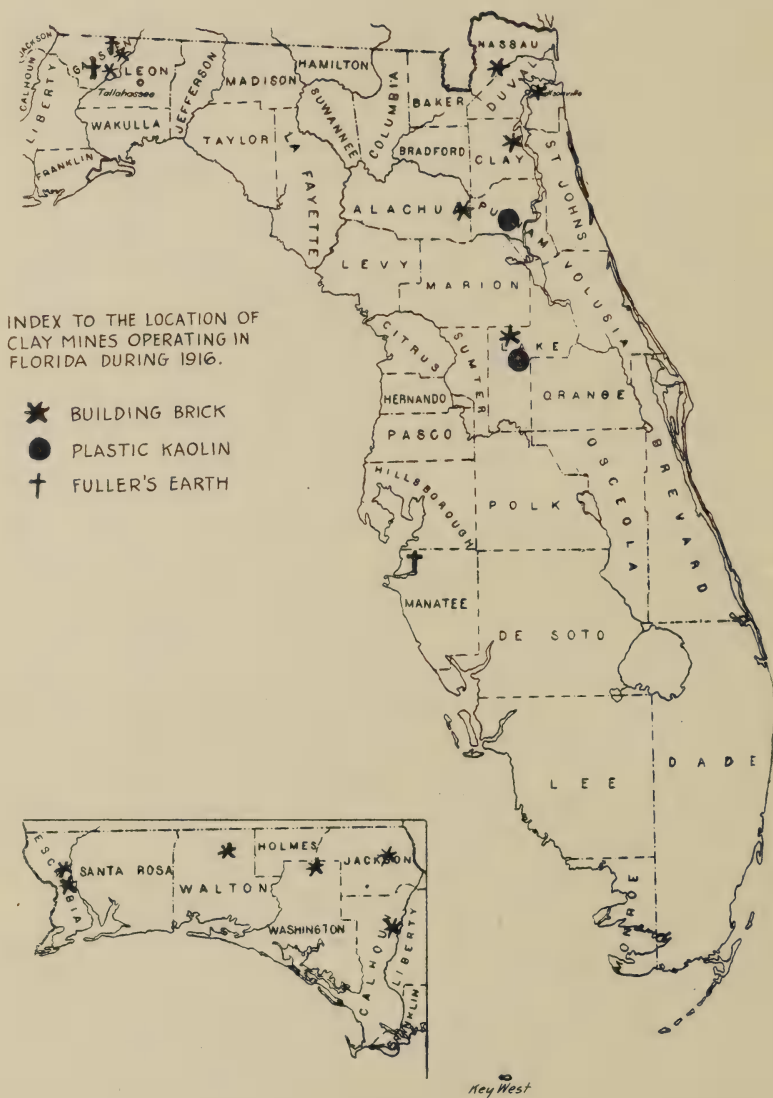


FIG. 1.

From the relay pumping station on the dredge the material passes through the washing station where the coarse sand and clay balls are removed to settling tanks. From the settling tanks the clay is again pumped into compressors. After the excess of moisture is removed by compression, the clay is further artificially dried for shipment.

All of the plastic kaolin produced in Florida is shipped out of the State and is used chiefly or entirely in mixing with other clays where it is of value because of being plastic as well as white burning and refractory. Chemical analyses of this clay have been previously published and are accessible. On the map, which accompanies this paper, is indicated the location of the plants in Florida which are producing this clay, and also the location of the brick clay and fuller's earth plants of the state. The bibliography which follows includes references to some of the relatively few papers that have been published on the Florida clays.

Ries, Heinrich, "Clays of the United States East of the Mississippi River," *U. S. Geol. Survey*, Prof. Paper No. 11, pp. 83-85 (1903).

Matson, George C., "Notes on the Clays of Florida," *U. S. Geol. Survey, Bull.* 380, 346-357 (1909).

Sellards, E. H., "Mineral Industries and Resources of Florida," Fla. State Geol. Survey, *Sixth Annual Rept.*, 1914, pp. 23-35.

Memminger, C. G., "Florida Kaolin Deposits," *Eng. Mining J.*, 57, 436 (1894).

AN ATTEMPTED HEAT BALANCE OF A CONTINUOUS KILN OF THE CHAMBER TYPE.

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The available ceramic literature at the present time shows a great scarcity of heat-balance data. The relatively long test periods necessary in securing authentic results has tended toward discouraging the collection of such data, the value of which has long been recognized. It is with the idea of "helping along the cause" which has been sustained by Bleininger,¹ Gelstharp² and Harrop,³ that the authors have decided to present this data to the Society. The tests were conducted on one of the kilns at the Alton plant of the Alton Brick Company, Alton, Ill.

The Kiln.—The kiln was of the chamber, moving fire type, having fourteen chambers arranged in one continuous row. Each chamber received its fire from one side only, working on the down-draft principle, the flames coming up over a bag-wall, spreading over the chamber and passing out through the floor. That half of the floor nearest the bag-wall was closed, the other half was open, thus providing for a good distribution of heat over the entire chamber. A connecting flue for carrying the hot combustion gases from chamber to chamber extended the full length of the kiln beneath the floor level. The waste combustion gases and waste water-smoking gases were led from each chamber by auxiliary flues which connected with the main waste-gas and main water-smoking flues through bell dampers, all being underground. These main flues were parallel with the kiln and each was provided with a fan for creating draft.

Water-smoking was accomplished by drawing the gases from the cooling chambers behind the fires through a sheet-steel flue supported about ten feet above the top of the kiln. (This is known

¹ *Trans. Am. Ceram. Soc.*, 10, 412 (1908); 11, 153 (1909).

² *Ibid.*, 12, 621 (1910).

³ *Ibid.*, 19, 216 (1917); *THIS JOURNAL*, 1, 35.

as the short-circuiting flue.) The gases pass down through the chambers which are water-smoking and out into the main water-smoking flue.

The fuel used, producer gas, was supplied through a large main flue extending the full length of the kiln, below the floor level and on the opposite side from the main water-smoking and main waste-gas flues. Distributing flues, one for each chamber, rose perpendicularly to the top of the kiln, at which point each led off at right angles into a horizontal flue which extended across the kiln, parallel to the axis of the chambers. These horizontal flues were integral with the kiln brick work and placed between the chambers. The gas was then delivered by small ducts to the foot of the bag-walls.

The Gas Producers.—The gas producers were in two batteries of four each, being of the simple or carbon-monoxide type. They were rectangular in plan with a single hopper at the top for feeding the coal. Two holes were provided in the side walls, through which a poker could be thrust for stirring up the fuel bed. No seal was used, the coals resting on horizontal grates at the bottom. The firing interval was fifteen minutes and the grates were cleaned every eight hours.

The Ware.—The wares burned were shale paving block and hard burned shale building brick, both maturing at about cone 4, or, to be exact, 1120°C . The pavers were wire-lug-cut and the builders were side-cut. The percentage of No. 1 ware produced was high, showing a good distribution of heat from top to bottom.

Testing Apparatus Used.

(a) **Gas Testing Apparatus.**—This consisted of a Burrell complete gas analysis outfit of the portable type, provided with pipettes for the determination of CO_2 , CO , O_2 , and unsaturated hydrocarbons by absorption and H_2 and CH_4 by combustion. Both the flue-gas and producer-gas were analyzed with this outfit.

(b) **Junker's Gas Calorimeter.**—It was planned to use this apparatus in obtaining the heating value of the producer-gas, but owing to adverse conditions the results could only be used as checks, the heating value being obtained by calculation.

(c) **Thermocouples.**—A noble metal couple was used for high temperature work and two base metal couples for obtaining the temperatures in the producer-gas and waste combustion-gas flues.

(d) **Gas Collecting Apparatus.**—In order to obtain true gas samples from the various flues and the interior of the burning chambers, pieces of $\frac{3}{4}$ " iron pipe were used. These varied in length from 6 to 9 feet, were closed at one end and bushed down at the other to take a 12-in. length of $\frac{1}{4}$ " pipe. Holes were drilled at random along the length of the $\frac{3}{4}$ " pipe, those nearest the bottom being larger than the ones at the top. The gas sample was drawn through these tubes into a large pressure tank. This pressure tank was designed similar to the large tanks used by gas companies. Its cubic capacity was about $2\frac{1}{4}$ cubic feet. In operation, the lower half was filled with water which had been saturated with the gas to be sampled. The upper half was then placed in position and lowered until the water started to flow from the intake pipe in its head. The tank was then connected to the sampling tube by a long piece of rubber hose. Then by raising the upper half of the tank a vacuum was created, the water forming a seal, and the gas flowing into the tank. By emptying and refilling the tank two or three times, a sufficiently pure sample was obtained. Then, if it was desired to use the Junker calorimeter for obtaining the heating value of the gas, all that was necessary was to connect the full tank to the calorimeter, the weight of the upper half of the tank being sufficient to maintain the proper pressure.

(e) **Thermometers.**—A centigrade thermometer was used in obtaining the temperature of the gas in the waste water-smoking flue and of the atmosphere. Wet- and dry-bulb thermometers were not used for obtaining the humidity of the air, as the test was carried on during a rain-storm and heavy mist, so that the relative humidity was 100 per cent.

The Heat Balance.

In making a heat balance on a producer-gas fired continuous kiln the following factors must be determined:

- A. Heat introduced as fuel.
- B. Heat lost by un-burned carbon in ashes.
- C. Heat lost in the producer.
- D. Heat used in the burning of the ware.
- E. Heat lost in the combustion-gases.
- F. Heat lost in water-smoking gases.
- G. Heat taken up by the kiln and lost by radiation.

In order to obtain the data for the above factors the following observations, analyses, etc., were made:

Methods Used in Obtaining Data.

1. Tons of Coal Used.—The weight of coal required to charge the hopper of the producer to each of three different depths was determined and subsequent charges were noted as $\frac{1}{4}$, $\frac{1}{2}$ and full hoppers. In each case the depth of charge was determined by measurement and recorded on a firing sheet. This process was continued for a complete cycle of the kiln, which covered a period of four hundred and seventy-eight hours. Knowing the weight of coal corresponding to each of the three depths, the total amount of coal used during the period was calculated.

This method must necessarily depend upon the intelligence of the firemen and the interest which they take in the work. Small errors will be of a compensating nature, so that large errors need only be guarded against.

2 and 3. Heating Value and Analysis of Coal.—An average sample of the coal was taken over a period of seventy-two hours. Each time the fireman fired his producer he threw a small quantity of coal on a pile. At the end of the period this pile was quartered to a small pile and gathered in a sampling can. This sample was analyzed by the Department of Applied Chemistry of the University of Illinois under the direction of Mr. J. M. Lindgren.

4. Analysis of Producer Ashes.—Each time the fireman cleaned the grates, he threw a small quantity of ashes onto a pile. This pile was quartered down and the sample gathered in a sampling can. This sample was also analyzed by the Department of Applied Chemistry, Univ. of Ill.

5 and 6. Analysis of Producer-Gas and Flue-Gas.—These analyses were made with a Burrell apparatus.

7. Temperatures of Gases in Producer-Gas and Waste-Gas Tunnels.—A base-metal thermocouple was inserted into the flue through an opening in the top and readings taken in millivolts with a portable Leeds and Northrup potentiometer equipped with compensation coils for the temperature correction of the cold junction of the thermocouple. The thermocouples were calibrated and the millivolt readings were transferred to temperature readings by interpolation from the calibration curves.

8. Maximum Burning Temperature.—A platinum-platinum rhodium thermocouple was inserted through the crown into the chamber on high fire. Readings were taken with a potentiometer.

9. Humidity of the Air.—As stated before, the relative humidity was 100 per cent., due to the fact that rain and heavy mist fell throughout the test.

10. Humidity of Waste Gases.—Due to the inaccessibility of the top of the waste-gas stack and the large volume of sulphur-gases coming from the stack, this determination was neglected.

11. Tons of Clay Burned.—The number of bricks or blocks set in each chamber was obtained from records in the company office. Ten blocks and ten bricks were weighed, to determine the average weight of each burned block or brick. From these weights and the number of blocks or bricks set in the kiln the tonnage of the kiln for the entire cycle was calculated.

12. Heating Value with Junker's Calorimeter.—This method is a direct method for obtaining the heating value of a gas. A known volume of gas is burned and allowed to heat a known weight of water, the temperature rise in the water being observed. From this data the heating value is calculated. Due to the fact that conditions were not favorable for the accurate working of the calorimeter—there being drafts blowing over the work-table, and a variable gas supply—these results were used only as a check, the calculated heat value being used throughout the work.

Method of Calculation.

The method of calculation employed followed the general method set down by Bleininger, Gelstharp and Kratz.¹ In specific cases the method was altered to suit the conditions of the data used.

The items to be calculated in the determination of the factors necessary for a complete heat balance such as this are:

- A. Heat Introduced as Fuel.
 - 1. Number of pounds of coal fired per ton of burned clay.
 - 2. Number of B. t. u. in coal used per ton of burned clay.
- B. Heat lost in un-burned carbon in ashes.
- C. Heat lost in gasification.
 - 1. Cubic feet of gas per pound of dry coal.
 - 2. Heating value of gas per cubic foot.
 - 3. Sensible heat in gas per pound of dry coal.
 - 4. Total heat in gas per pound of dry coal.
- D. Heat used in burning the ware.
 - 1. Heat used in driving off hygroscopic water.
 - 2. Heat used in dehydrating the clay.
 - 3. Heat used in heating up clay substance.
- E. Heat lost in the combustion-gases.
 - 1.* Cubic feet of flue-gas per cu. ft. of producer-gas.
 - 2. Cubic feet of flue-gas per pound of dry coal.
 - 3. Sensible heat in flue-gas per pound of dry coal.
- F. Heat lost in water-smoking gases.
 - 1. Cubic feet of gases per pound of dry coal.
 - 2. Sensible heat of gases per pound of dry coal.
- G. Heat absorbed by kiln and lost by radiation.

A. Heat Introduced as Fuel.—This was calculated on the basis of pounds of coal per ton of ware burned. The total weight of coal used was divided by the total tonnage of the kiln. This gave the pounds of coal used per ton of ware. Multiplying this result by the heating value of the coal per pound as fired gave the heat introduced.

B. Heat Lost in Unburned Carbon in Ashes.—The percentage of unburned carbon in the ashes was obtained from the analysis

¹ Garland and Kratz, "Tests of a Suction Gas-Producer," Eng. Exp. Sta., Univ. of Ill., *Bull.* 50.

of the ashes. Since the earthy matter in the ashes corresponds to the "ash" of the coal, the unburned carbon in the ashes per pound of coal is readily obtained. The total ashes per pound of coal equals 100 per cent. divided by the percentage of ash in the ashes and multiplied by the percentage of ash in the coal. This, multiplied by the percentage of carbon in the ashes, gives the percentage of unburned carbon in the ashes in terms of one pound of coal. Multiplying this result by the heating value of carbon per pound gives the heat lost.

C. Heat Lost in Gasification.—Since the basis of the efficiency calculations is one pound of dry coal, the volume of producer-gas per pound of dry coal must be first obtained. The weight of carbon combined in CO_2 , CO , and CH_4 per cubic foot of producer-gas is calculated from the per cent. compositions. The weight of carbon burned on the grate per pound of coal is the difference between the per cent. of carbon in the coal and the per cent. of un-burned carbon in the ashes in terms of one pound of coal. This difference, divided by the weight of carbon per cubic foot of gas, gives the volume of gas per pound of dry coal.

The heating value of the gas per cubic foot is calculated from the per cent. composition and heating value of the combustible constituents. In obtaining the total heat of the gas per cubic foot, it is necessary to add to the heating value, the sensible heat at the temperature at which the gas enters the kiln. This is obtained from the per cent. composition, the specific heat of the constituents, and the temperature. Multiplying the total heat per cubic foot by the cubic feet per pound of coal gives the heating value of the gas per pound of coal. This value, subtracted from the heating value of one pound of coal, gives the heat lost by gasification.

D. Heat Used in Burning the Ware.—In this calculation it is assumed that the clay contains 2 per cent. hygroscopic water and three per cent. of chemical water. The total heat absorbed is, therefore, the heat used in driving off and turning into steam the hygroscopic and chemical water plus the heat used in burning the clay substance. The latter is obtained by multiplying

the weight of clay by the specific heat of clay and multiplying this result by the temperature rise.

E. Heat Lost in Combustion-Gases.—The volume of flue-gas per cubic foot of producer-gas is obtained by dividing the weight of carbon in the producer-gas per cubic foot by the weight of carbon in the flue-gas per cubic foot. This result, multiplied by the cubic feet of producer-gas per pound of dry coal, gives the volume of flue-gas per pound of dry coal. From the per cent. composition of the flue-gas, the specific heats of the constituents at the flue-gas temperatures, the temperature of the flue-gas, and the volume of flue-gas per pound of coal, the heat lost in the combustion-gases is readily calculated.

F. Heat Lost in Water-smoking Gases.—Due to the fact that the water-smoking gases left the flue at approximately atmospheric temperature, this loss was negligible and was not taken into account.

G. Heat Absorbed by Kiln and Lost by Radiation.—As the factors which enter into this calculation are so variable and the data so difficult to obtain, it is determined by the difference between 100 per cent. and the summation of the calculated factors in the heat distribution. It is plainly evident that radiation will be small in this type of kiln—due to the great thickness of the walls, the small areas subjected to high temperatures at any one time, and the high velocity with which the gases are moving through the kiln.

Data.

Coal used, as obtained from data sheets and recorded	
by producer firemen.....	524,728 lbs.
B. T. U. value of coal per pound by combustion in oxygen	
bomb calorimeter and furnished by the University of	
Illinois, Department of Applied Chemistry. Dry basis...	12,630
As received...	11,175
Tonnage of burned clay in the 14 chambers.....	1743.0 tons
Coal used per ton of burned clay.....	301.0 lbs.
Coal used per 1000 blocks.....	1400.0 lbs.
Coal used per 1000 builders.....	834.0 lbs.
Average weight of blocks.....	9.3 lbs.
Average weight of builders.....	5.7 lbs.

Average temperature of producer-gas flue.....	708° F.
Average temperature of waste-gas flue.....	406° F.
Average temperature of water-smoking flue.....	60° F.
Average temperature of atmospheric air.....	60° F.
Maximum temperature of burning.....	1120° C.

Analysis of Coal.

	Ultimate.		Proximate. Dry.	As received.
C.....	69.90	Fixed carbon.....	41.30	37.30
H ₂	4.95	Volatile matter.....	44.48	38.58
O ₂	10.29	Moisture.....	0.00	11.53
N ₂	0.62	Ash.....	9.52	8.43
S.....	4.71	Sulphur.....	4.71	4.17
Ash.....	9.52			

Analysis of Ashes.

C	=	22.24
Ash	=	77.78

Average Gas Analysis (samples taken over a period of 72 hrs.).

Producer-gas.	Flue-gas.
CO ₂ = 4.3	CO ₂ = 3.5
CO = 24.4	O ₂ = 17.1
CH ₄ = 1.5	N ₂ = 79.5
H ₂ = 7.4	
O ₂ = 0.6	
N ₂ = 62.1	

Calculations.

Calculation of Producer Efficiency.—For each cubic meter of CO₂, CO and CH₄ $\frac{12}{22.4}$ kilograms of carbon are required.

$$0.043 \times \frac{12}{22.4} = 0.023 \text{ Kg. of C in CO}_2 \text{ per M}^3 \text{ of gas.}$$

$$0.244 \times \frac{12}{22.4} = 0.131 \text{ Kg. of C in CO per M}^3 \text{ of gas.}$$

$$0.015 \times \frac{12}{22.4} = 0.008 \text{ Kg. of C in CH}_4 \text{ per M}^3 \text{ of gas.}$$

$$0.162 \text{ Kg. of C in one M}^3 \text{ of gas.}$$

$$\frac{0.162 \times 2.2}{35.25} = 0.0101 \text{ lb. of coal per cu. ft. of gas.}$$

Carbon per lb. of coal from analysis = 0.6990 lb.

$$\text{Unburned Carbon in Ashes per Lb. of dry coal} = \frac{100}{77.76} \times 0.0952 \times 0.224 = 0.0272 \text{ lb.}$$

$$\text{Volume of producer gas per lb. of dry coal} = \frac{0.6990 - 0.0272}{0.0101} = 66.5 \text{ cu. ft.}$$

Heating Value of Gas.

$$0.244 \times 323.5 = 79.9 \text{ B. T. U. in CO per cu. ft. of gas.}$$

$$0.074 \times 326.2 = 24.1 \text{ B. T. U. in H}_2 \text{ per cu. ft. of gas.}$$

$$0.015 \times 1009.2 = 15.1 \text{ B. T. U. in CH}_4 \text{ per cu. ft. of gas.}$$

$$\text{Total, } 119.1 \text{ B. T. U. per cu. ft. of gas.}$$

Sensible Heat in Gas.

$$0.043 \times 0.0257 \times 708 = 0.82 \text{ B. T. U. in CO}_2.$$

$$0.96 \times 0.0177 \times 708 = 12.00 \text{ B. T. U. in CO, O}_2, \text{CH}_4, \text{H}_2 \text{ and N}_2. \\ 12.82 \text{ B. T. U. per cu. ft. of gas.}$$

Total Heat of Producer-Gas per Pound of Dry Coal.

$$12.82 \times 66.5 = 852 \text{ B. T. U. sensible heat}$$

$$119.1 \times 66.5 = 7920 \text{ B. T. U. at atmospheric conditions}$$

$$8772 \text{ B. T. U. total heating value of gas per lb. dry coal.}$$

$$\frac{8772}{12630} \times 100 = 69.4 \text{ per cent.} = \text{efficiency of the producers.}$$

Per Cent. Heat Lost by Unburned Carbon in the Ashes =

$$\frac{0.0273 \times 14600 \times 100}{12630} = 3.15 \text{ per cent.}$$

Per Cent. Heat Lost by Gasification in the Producers =

$$100 - (69.4 - 3.15) = 27.45 \text{ per cent.}$$

Thermal Efficiency of the Kiln.

$$\text{Maximum temperature of burning} = 1120^\circ \text{ C.}$$

$$\text{Average atmospheric temperature} = 20^\circ \text{ C.}$$

$$\text{Temperature rise of clay in chambers} = 1100^\circ \text{ C.}$$

$$\text{Heat of dehydration of clay}^1 = 200 \text{ G. cal. per G. of water.}$$

$$\text{Latent heat of hygroscopic water}^1 = 476 \text{ G. cal. per G. of water.}$$

¹Clay is assumed to contain 2 per cent. hygroscopic water and 3 per cent. chemical water.

Hygroscopic water leaves at 200°C .

Dehydration temperature of clay = 650°C .

The specific heat of clay = 0.200.

Distribution of Heat in Clay.

Hygroscopic water.....	0.02	\times	180	\times	1	=	3.6 Kg. cal.
	0.02	\times	478			=	9.5 Kg. cal.
Chemical water.....	0.03	\times	0.02	\times	650	=	3.9 Kg. cal.
	0.03	\times	200			=	6.0 Kg. cal.
Clay.....	0.97	\times	0.200	\times	1100	=	213.4 Kg. cal.

Total heat required by 1 Kg. of clay = 236.4 Kg. cal.

236.4 Kg. cal. = 425 B. T. U. per lb. of clay.

1 ton of clay requires $2000 \times 425 = 850,000$ B. T. U.

Heat introduced as coal per ton of clay = $301 \times 11175 = 3,363,675$ B. T. U.

Efficiency of kiln in terms of coal used at the producers =

$$\frac{850,000}{3,363,675} = 25.3 \text{ per cent.}$$

Efficiency of Kiln in Terms of Dry Coal. $\frac{11175}{12630} \times 25.3 = 22.3$.

Percentage of Heat Used in Burning Ware = 25.3 per cent.

Heat Lost in Waste-Gas Flue.

$0.244 \times 1 = 0.244$ cu. ft. of CO_2 from CO per cu. ft. of gas.

$0.015 \times 1 = 0.015$ cu. ft. of CO_2 from CH_4 per cu. ft. of gas.

$0.043 \times 1 = 0.043$ cu. ft. of CO_2 from CO_2 per cu. ft. of gas.

0.302 cu. ft. of CO_2 in combustion-gas from 1 cu. ft. of producer-gas.

0.035 per cent. of CO_2 actually in combustion-gas from analysis.

$$\frac{0.302}{0.035} = 8.63 \text{ cu. ft. of combustion-gas from 1 cu. ft. of producer-gas.}$$

$8.63 \times 0.036 \times 66.5 = 20.1$ cu. ft. CO_2 per lb. of coal.

$$8.63 \times 0.171 \times 66.5 = 92.2 \text{ cu. ft. O}_2 \text{ per lb. of coal.}$$

$$8.63 \times 0.795 \times 66.5 = 456.0 \text{ cu. ft. N}_2 \text{ per lb. of coal.}$$

$$0.074 \times 0.5 \times 66.5 = 2.5 \text{ cu. ft. of water per lb. of coal from H}_2.$$

$$0.015 \times 2 \times 66.5 = 2.0 \text{ cu. ft. of water per lb. of coal from H}_2.$$

$$2000 \times 0.03 = 60 \text{ lbs. of water per ton of clay.}$$

$$\frac{60}{301} = 0.20 \text{ lb. of water per lb. of coal from the clay.}$$

$$0.20 \times \frac{22.4}{18} \times 1.31 \times 27 = 8.8 \text{ cu. ft. of water per lb. of coal,}$$

from the clay.

$$13.3 \text{ cu. ft. of water in gas per lb. of coal.}$$

$$20.1 \times 0.0248 \times 406 = 201 \text{ B. T. U. in CO}_2 \text{ per lb. of coal.}$$

$$554.2 \times 0.0175 \times 406 = 3940 \text{ B. T. U. in O}_2 \text{ and N}_2 \text{ per lb. of coal.}$$

$$13.3 \times 0.022 \times 406 = 119 \text{ B. T. U. in H}_2\text{O per lb. of coal.}$$

$$\text{Total heat lost in flue-gas} = 4260 \text{ B. T. U. per lb. of coal.}$$

$$\frac{4260}{12630} = 33.7 \text{ per cent. heat lost in flue-gas.}$$

Heat Absorbed by Kiln and Lost by Radiation.—100 —

$$(3.15 + 27.45 + 22.3 + 33.7) = 13.4 \text{ per cent.}$$

Summary.

	Per cent.
Heat lost by carbon in the ashes.....	3.15
Heat lost by gasification in the producer.....	27.45
Heat used in burning the ware.....	22.3
Heat lost by waste-gas.....	33.7
Heat lost in water-smoking gases.....	0.0
Heat lost by radiation and conduction.....	13.4

Total, 100.00

While we are skeptical as to the exactness of the data obtained and the reliability of some of the constants used in the calculations, we feel that a method is given which, with variations to suit the conditions demanded, is very well suited for the obtaining of data for a heat balance on any type of movable fire continuous kiln.

In conclusion, we wish to express our indebtedness to Mr. F. J. Hoehn for the standardization of the couples used, Mr.

R. K. Hursh for suggestions, and Mr. E. B. Rodgers, of the Alton Brick Co., for his hearty coöperation in the work.

COMMUNICATED DISCUSSIONS.

C. B. HARROP: In reading over this paper, I have been particularly interested in the figures covering kiln efficiency and heat used in burning the ware.

In calculating the "efficiency of the kiln in terms of coal used at the producers," the ratio $\frac{850,000}{3,363,675}$ is used giving an efficiency of 25.3 per cent. The numerator is calculated on the basis of 1.02 tons of green clay (including its hygroscopic water), instead of 1.052 tons of green clay (which equals 1 ton of burned clay), while the denominator is calculated clearly on the basis of 1 ton of dry clay. Recalculating this on the basis of 1.052 tons of green clay, as equalling 1 ton of burned clay, gives an efficiency of 26.1 per cent. instead of 25.3 per cent. Furthermore, this figure should not be called the efficiency of the kiln, but rather the efficiency of the kiln and producers, as part of the inefficiency is due to the particular producers employed and is not a function of the kiln.

These are small matters, however, when there comes up the difficult question of what should constitute the value of the numerator in the efficiency ratio. Mechanical efficiency is the ratio of out-put to in-put. Thermal efficiency should probably be regarded as the ratio between the amount of heat put to useful purpose (or actually doing necessary work) and the total heat applied. The question immediately arises as to what constitutes this useful purpose. If a chimney were being employed to supply kiln draft, the stack gases should have a temperature of from 400° to 600° F. If the stack temperature were reduced, by carrying the products of combustion through additional chambers, to a temperature just high enough to create the requisite draft, the heat then contained in the stack gases should certainly be considered as useful, for without it the kiln could not operate. On the other hand, any heat in excess of this would be wasted.

Even if the water-smoking gases left the kiln at 500° F. but completely saturated, this heat would represent a necessary work and should not be considered a waste or loss. On the other hand, if the water-smoking gases were not saturated, the heat represented between their temperature and the dew point would be a loss, while the difference between this loss and the total amount of heat carried would be useful.

Referring again to the calculation showing that the "percentage of heat used in burning the ware equals 25.3 per cent.," the data taken during the test show that 301 pounds of coal were burned at the producers for every ton of ware out-put. In other words, considering units and thinking of only the fundamentals of the burning operation—we set 1.05 tons of green ware at atmospheric temperature; we fire 301 lbs. of coal, then we remove one ton of burned ware at atmospheric temperature. What heat work has been accomplished? Merely that which is incident to the elimination of hygroscopic water, dehydration of the clay, and certain other pyro-chemical changes within the clay mass. If the ware had been removed from the kiln at the maximum temperature of 1120° C., then the author's calculation would have been proper—but instead of being removed from the kiln this heat was transferred by radiation, conduction, and convection (principally the latter) to the preceding chambers.

To state it differently the calculation shows that 25.3 per cent. of the heat in 301 lbs. of coal is used in burning one ton of the ware and the difference ($100 - 25.3$), 74.7 per cent. is wasted or lost. If this is true, and 25.3 per cent. of all the heat from the producers finds its way into the ware at its highest temperature in each and every chamber, then what becomes of the heat as these chambers of ware cool? It cannot be wasted or lost—because the 74.7 per cent. of heat from the producers covers that. The error is apparent and very large.

Using the author's figures, the "percentage of heat used in burning the ware" should be based on the heat used in driving off the hygroscopic water and dehydrating the clay and should not include any sensible heat in the ware as a result of temperature attained in the kiln.

There is one other probable source of error in this same connection, namely, the failure to include the heat required to evaporate the mechanical water in the ware when set. This usually amounts to from 1 to 3 per cent. or more—even after having passed through a good drier.

C. TREISCHEL: I have very carefully noted Mr. Harrop's discussion of this paper and, after re-checking the data, find that there is an error in the kiln efficiency calculation as he has shown.

With reference to the remainder of the discussion, however, I am obliged to take exception. Efficiency is the "ratio between out-put and in-put." Thermal efficiency, we agree, is the "ratio between the heat put to necessary work and the heat in-put." But what is the necessary work with reference to this particular kiln? The draft is produced mechanically. Is it necessary for a draft fan to operate on a gas mixture at 400° F. in order to produce draft? If not, what is the temperature? I have seen several kilns having mechanical draft in which the temperature of the waste-gases was very near atmospheric temperature. Unfortunately, there is no data available to show whether or not these kilns were more efficient than the one described in our paper. However, the operators of two of these kilns have told me that when the waste-gases leave at a higher temperature, their kilns burn more coal. If this be true, and I have every reason to believe it is true, then, if the same facts will apply to the kiln in question, all the heat leaving from the waste-gas flue above that leaving at atmospheric temperature is a loss.

There is practically no loss in the water-smoking operation—due to the fact that the gases leave at a high humidity and at atmospheric temperature.

Now then, are we much in error when we say that this kiln is only 25.3 per cent. efficient? The heat lost by gasification in the producers and in the un-burned carbon in the ashes must be called a loss. The heat leaving the kiln with the flue-gases must be regarded as lost. There remains then only the loss through radiation, etc., which is not unreasonable when one considers the thickness of the walls, crown insulation, and all other details of con-

struction of this type of kiln. Disregarding small errors, the general method of procedure seems correct.

Then, looking at the proposition from a practical standpoint, the kiln uses 201 pounds of coal in producing one ton of ware—25.3 per cent. of the fuel being used in the actual burning. As this ton of ware cools, the heat is drawn off and put to some other purpose, such as heating the ware in the preceding chambers—the operation being continuous. If this were not done the 301 pounds of coal might become 500 lbs., or even 600 lbs., per ton of ware, in which case the efficiency would be materially reduced.

NOTES ON THE LABORATORY TESTING OF SILICA BRICK.

BY R. J. MONTGOMERY AND L. R. OFFICE, Pittsburgh, Pa.

The importance of the accurate testing of silica brick is receiving more and more attention as is indicated by the number of articles written on the subject and the amount of work being done at the various ceramic laboratories. This discussion is intended to cover certain tests that are now quite commonly employed in determining the quality of silica brick, and in order to present the experience of the authors as an addition to the data so far published.

The recent unusual demand for silica brick has placed upon the market a number of new brands and has led to the investigation of various kinds of raw materials in order to determine their suitability for the manufacture of silica brick. In addition to the typical ganister rock, a number of other silicious materials such as chert, sand rock, and materials which grade from a fair ganister to quartz sand, loosely bonded together, are being tried. At present, there are at least two grades of silica brick on the market. The line between these grades is not sharp and their classification would vary with the purposes for which the brick are used. In a classification based upon the fusion point, we could say that Grade A would fuse at cone 32 or above and that Grade B would fuse below cone 32.

In the testing of silica brick, it must be remembered that they differ from fire clay brick in that they are composed almost entirely of one substance, silica. Therefore, the properties of the silica used govern the properties of the silica brick—this being kept in mind in the following discussion of certain important points in the testing of silica brick:

1. Raw Materials.—The recognized ganister rocks are known to be capable of being manufactured into silica brick of high quality, while the quality of brick manufactured from the other

kinds of silica rock is still open to question. Undoubtedly, for many purposes, the one class of material will answer as well as the other—if the brick are properly manufactured and the raw silica is of uniform quality. A picked sample of sand rock or chert may have a silica content of 96 per cent. or above, but in handling, clay and other impurities are likely to be included and the refractoriness of the brick may thus drop below cone 32. Another point of importance to be considered in selecting the silica is the physical strength of the brick after burning. Ganister rock crushes down into splintery fragments and the brick has a higher crushing strength in the cold condition than does a brick from sand rock which crushes to rounded grains. In manufacture, the sand rock brick are burned from 3 to 4 cones lower than are the ganister brick. It is possible that a sand rock brick, in which the impurities present act as a bond, although having a lower fusion point would give a brick as strong physically as one made from crushed ganister rock, providing it were burned to the proper cone. This, however, would increase the physical strength at the expense of a lower softening point.

2. Visual Inspection.—Field and factory inspection can do much to insure uniform quality after the raw silica has been found satisfactory. Manufacturing defects will always be present. Cracked and spongy brick are easily rejected and under-burning may be detected by linear measurements and tapping with a hammer. After the desired expansion in burning has been established, careful measurement will detect any serious under-burning. The measurement test, however, is not entirely satisfactory and should be supplemented by laboratory tests.

3. Chemical Analysis.—The chemical analysis is of great assistance in determining the purity of the raw material used and should be considered in connection with an actual inspection of the silica deposit or the raw material at the plant. For control work the value of chemical analyses is doubtful. To secure reliable analytical results the services of a high-grade chemist are necessary and this makes the analytical work very expensive. Tests other than the chemical analysis may be used as a check on uniformity.

4. **Deformation Test.**—The ordinary deformation test, using standard pyrometric cones for comparison, is of value. A silica brick of the best quality, made from pure ganister, will not soften below cone $32\frac{1}{2}$ or 33. Practically all of the brick made from chert or sand rock have a softening point of from cone 31 to 32. The softening temperature of a highly silicious material is not sharply defined and the determination is difficult owing to the high viscosity of the softened material.

5. **Load Test.**—The load test for silica brick, as recommended by the American Society for Testing Materials, specifies a load of 25 lbs. per sq. inch at a temperature of 1500°C . Very few failures have been recorded under these conditions and it is a question whether the test is of value unless for the testing of new brands of brick. When failure occurs, it is due to shearing or a rupture of the bond and not to a softening of the whole brick.



FIG. 1.

In Fig. 1 is shown a typical failure of a silica brick under the load test.

A very interesting curve is obtained from a continuous record of the expansion and contraction of a silica brick during the load test. In Fig. 2 is shown the theoretical expansion curve as given by J. Spotts McDowell¹ and the actual expansion curve as de-

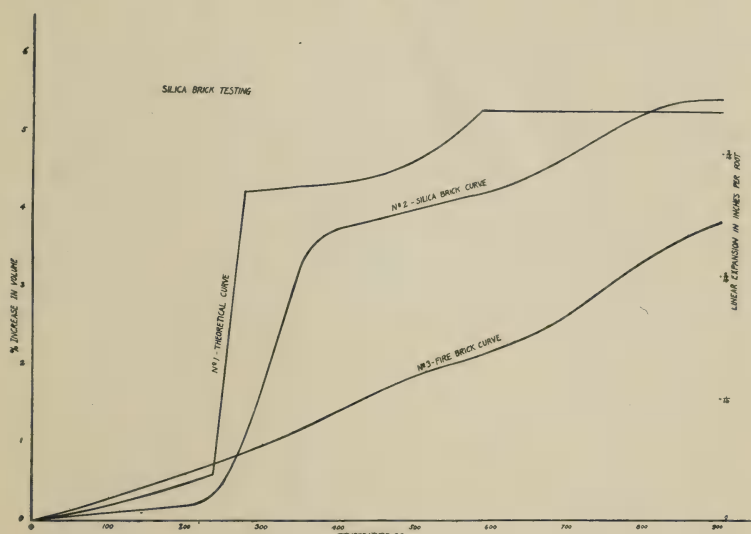


FIG. 2.

terminated in a load test. A curve showing the behavior of a clay fire brick under load is also given. The data from which curves 2 and 3 were plotted was not definitely determined but the general trend of the curves is unquestioned.

6. Crushing Strength.—The crushing strength (cold) of a silica brick (on end) has often been used as a measure of the quality of the bond. The crushing strength of the different brands varies from 900 lbs. per sq. in. as a minimum to 3700 lbs. per sq. in. as a maximum, the average being from 1800 to 2800 lbs. per sq. in.

¹ *Bull. Am. Inst. Mining Eng.*, p. 2044, November 1916 (No. 119).

7. Specific Gravity.—D. W. Ross¹ has proven the value of the specific-gravity determination in the detection of under-burned silica brick. The method for making this determination is the one used for the apparent sp. gr. of ceramic materials—the apparent sp. gr. of a silica brick being quite close to its true sp. gr. Using a 20-gram sample and boiling for one hour to obtain saturation has been found to be satisfactory and as accurate as the two-inch cube recommended by Mr. Ross. Check determinations should be made to guard against error.

The sp.-gr. determination undoubtedly detects under-burning. Samples taken from 14 separate cars of silica brick, known to have been burned from cone 15 to 16, gave an average sp. gr. of 2.42, while samples from 12 separate cars of brick known to have been burned to cone 18 gave 2.36. Four samples of brick, thought to be under-burned, were re-burned to cone 20 and tested. The results were as follows:

No.	Before re-burning. Sp. gr.	After re-burning. Sp. gr.
1	2.44	2.38
2	2.40	2.36
3	2.39	2.36
4	2.43	2.36

8. Porosity.—The variation in the porosities of burned silica brick is slight and little use can be made of this determination. The porosity of most silica brick varies from 22 to 29 per cent.

Quite a number of other tests such as slagging, spalling, impact, etc., have been used but the authors have not enough information to warrant their detailed discussion.

Effect of Impurities.

Lime.—The lime content of silica brick is well defined, about 2 per cent. being necessary. If the lime content is less than 2 per cent. the bond will be weak and, if higher, the refractoriness of the brick will be lowered.

Alumina.—Alumina, introduced in the form of clay or other silicates, is probably the most active of all the fluxing impurities present in a silica brick. It should not exceed 1.50 per cent. Its

¹ *Trans. Am. Ceram. Soc.*, 19, 83 (1917).

presence in excess of this amount is easily detected by a softening point below cone 32. Although a low softening point is not proof of an excessive alumina content—it should be the first impurity looked for.

Iron.—Ordinary iron discoloration seems to have less effect on the refractoriness of a silica brick than would be expected. The iron present seems to become saturated with silica and remain relatively inactive. The actual color depends considerably upon the degree of oxidation. A chemical analysis of a dark brown section of a silica brick gave 4.83 per cent. Fe_2O_3 . This sample was heated to 2800°F . and held at this temperature for one hour. No spreading or local fusion was in evidence.

Two small chips from a brick showing iron spots were heated to cone 32 started or just below the softening point of the brick. The iron color seemed to distribute slightly but increased fusion or slagging was not observed. A badly discolored chip from a brick softened at about cone 32 or about half a cone below the normal softening temperature. Although the content of iron should not, in most cases, exceed 1.5 per cent., the importance of the presence of this impurity in silica brick has been exaggerated—due to its high coloring power.

The other impurities which are found present in very small amounts in silica brick are usually not considered.

Safe Operating Temperatures for Silica Brick.

There is a tendency to claim a very high operating temperature for silica brick, and statements are often made that a silica brick will not soften at 3100° or 3200°F . Statements of this kind should be qualified somewhat since in actual practice the bricks are subjected to the higher temperatures on one side only, the other side being much cooler. Owing to its high conductivity, the whole brick does not reach the temperature of the furnace—the heat being conducted away rapidly.

In order to obtain some information on this subject the following tests were made: A 3" by 3" by 9" section from each of two shape bricks, manufactured by two of the largest companies in the country, were heated to 2900°F . and held at this tem-

perature for 24 hrs. The temperature during the run did not vary more than 25°F. above or below 2900°F. Both bricks softened and slumped down to the bottom of the furnace. In Fig. 3 is shown the condition of these bricks after the test.



FIG. 3.

The test was repeated at 2800°F. and the bricks showed no fusion, the only effect being a whitening of the surfaces. The bricks were tested in a laboratory furnace and were exposed to the furnace temperatures from all sides—the entire mass thus attaining a practically uniform temperature. This indicates that silica brick may be subjected to higher temperatures when laid in a furnace wall in actual practice but the factor of safety lies only in the fact that the bricks do not attain this temperature throughout.

LABORATORIES OF THE H. KOPPERS CO.
AND PITTSBURGH BY-PRODUCT COKE CO.

COMMUNICATED DISCUSSIONS.

A. A. KLEIN: The authors are correct in stating that the properties of the raw silica dominate the properties of the silica brick. The complex thermal behavior of the quartz, including the modifications in which the silica is usually present in the raw material and the modifications of the silica resulting from the heat treatment, account for the peculiar properties of silica brick, for example—permanent expansion, spalling, etc.

The chemical analysis of a burned brick is of little assistance in a determination of the value of the brick—since it does not distinguish between the percentages of the various modifications of silica present. The importance of this point was shown forcibly in an investigation by the writer of the constituents of various standard brands of silica brick. The chemical analyses of the brands examined were found to show no great variations but the mineral constituents varied from, for instance, about 20 per cent. of unchanged quartz remaining in the best brick to about 80 per cent. quartz in the poorest one. In some cases, large differences in constituents were found where not only were the analyses similar but also where the same ganister formation served as the source of the raw material.

The importance of determining the constituents is evident from the great difference in the densities of the three silica modifications. These have been accurately determined by many investigators and there is no question as to the large expansion taking place when quartz inverts to cristobalite. The practical application of this is evident. If bricks contain a considerable percentage of unchanged quartz after being burned, and are used under conditions where the temperature reaches 1250° C. or higher, the inversion of the quartz in the bricks continues to a greater or lesser degree—depending upon the temperature. The expansion of the bricks keeps pace with this inversion until a dangerous condition of strain occurs—often resulting in great material damage.

It is therefore essential that a direct or indirect quantitative determination of the constituents be made. The easiest way is to obtain the apparent specific gravity of the brick—which

gives an accurate idea of the amount of unchanged quartz remaining and thus measures how much expansion has been "burned out" of the brick. This test is a most important one.

Although the chemical analysis of a burned brick is of little importance, the fact remains that it may be used, with reservations, to determine whether a raw material is suitable for silica brick-making. The authors speak of impurities causing a lowering of the refractoriness. It must be emphasized here that a silicious raw material may also be too pure. Perhaps an analogy, drawn outside the field of silica brick, would be a comparison between the Austrian and California magnesites used in the manufacture of magnesite brick.

To illustrate the effect of over purity, in a case the writer has in mind a certain quartzite containing 98 per cent. silica was used in making silica brick. It was found that, although the burning had caused sufficient quartz inversion, the bricks were "punk" and weak—due to the fact that there was not sufficient flux present to completely bond the silica grains.

It is safe to state that a rock suitable for silica brick manufacture should contain approximately 95 per cent. SiO_2 , but it is well to caution against the thought that any rock having this silica content is satisfactory for this purpose. Other factors must be taken into consideration—for example—the nature of the impurities, the structure of the rock, etc.

In conclusion, the writer is of the opinion that the statement "under-burning may be roughly checked by linear measurements and tapping with a hammer," made by the authors, under the heading "Visual Inspection," should be qualified. Measuring the brick will give rough checks only with bricks made at the same plant and compared to the same standard. It has been the writer's experience that very little reliance can be placed on the "ring" of a silica brick as indicating under-burning—since well-burned and under-burned bricks may have the same ring or the same lack of ring.

R. M. HOWE: Much valuable information is given by the authors of this paper—their points concerning the inspection of the raw material and the finished product being particularly

important. One man at a plant, who examines a bit of questionable raw material, who sees the cones fall during burning, who observes the care exercised during the process and how carefully the bricks are sorted, can tell more about the quality of the silica brick than a good-sized laboratory staff. His work is largely that of control and, knowing exactly what he seeks, his services are invaluable to the consumer. This is especially true when his observations are supplemented by a laboratory.

The points made by the authors in regard to the chemical analyses are well taken—as one cannot interpret the analytical results more than approximately. A silica content of 96.0 per cent., however, is rather unusual and should not be considered a necessity.

A few typical analyses of silica brick of acknowledged quality and which are the average of a large number of determinations, are given as follows:

	1.	2.	3.	4.	5.
Silica.....	96.05	95.85	94.96	95.58	95.31
Alumina.....	0.88	1.10	1.19	0.85	1.34
Iron oxide.....	0.79	1.04	0.85	1.26	1.31
Lime.....	1.80	1.80	2.02	1.77	2.04
Magnesia.....	0.14	0.20	0.22	0.25	0.11
Alkalies.....	0.39	0.15	0.38	0.13	0.27

From the above analyses it is apparent that many high grade ganister bricks contain less than 95.0 per cent. of silica. Analysis No. 1 is of a particularly pure brand of silica brick. An average silica content of 94.5 per cent. is hardly too low for a good grade of silica brick.

Softening points and load tests made on silica brick are of little value. The softening points do not vary more than 2 cones and the brick generally support a load of 25 pounds per square inch at 1500° C. Any which do not may be eliminated by other tests.

The crushing strength test on silica brick gives a large amount of information and can be verified by the modulus of rupture test—the latter not requiring such a large testing machine. These tests distinguish between well and poorly made brick, soft and hard burned brick, good and poor burning silica-bearing ma-

terial (some form a punky structure when burned), and proper and improper lime content, etc. They also serve to detect, qualitatively, the presence of any clay and other fluxes which may produce a firmer bond than ordinarily encountered.

The specific-gravity test must be conducted with care. It is generally sufficient to boil the test pieces in water at atmospheric pressure. However, the following results show that ordinary boiling is sufficient in one case and not in another: Each figure represents the average of four determinations made on samples taken from the same brick (the weight of the samples varying from 20 to 30 grams).

Brand.	Boiling $\frac{1}{2}$ hr. and standing 16 hrs. in water.	Boiling 1 hr. at atmo- spheric pressure.	Boiling 3 hrs. at atmo- spheric pressure.	Boiling 3 hrs. and then 1 hr. in vacuum.
Sample No. 1.	2.212 sp. gr.	2.357 sp. gr.	2.367 sp. gr.	2.333 sp. gr.
Sample No. 2.	2.165 sp. gr.	2.312 sp. gr.	2.322 sp. gr.	2.320 sp. gr.

The following determinations also show that boiling under a vacuum for 45 minutes is about equivalent to boiling 3 hours at atmospheric pressure and then one hour in a vacuum:

	Boiling 3 hrs. at atmospheric pressure and 1 hr. in a vacuum	$\frac{3}{4}$ hr. boiling in a vacuum
Sample No. 1.	2.333 sp. gr.	2.356 sp. gr.
Sample No. 2.	2.320 sp. gr.	2.316 sp. gr.
Average.	2.327	2.336 sp. gr.

In the cases cited, there is evidence that sample No. 1 also needed a more thorough boiling. It was also the one which was not saturated by boiling 3 hours in air at atmospheric pressure.

It is surprising to note that a re-heating test is not mentioned by the authors. The specific-gravity test is of particular value in indicating the relative conversion of quartzite into cristobalite and tridymite and, incidentally, how well the expansion has been "burned out" of the brick. This expansion is really the important factor and can be determined directly by re-heating a sample for five hours at 1400° C.

The authors evidently distinguish between general tests and control tests. General tests include the chemical analysis, visual

inspection, load test, softening point test, specific-gravity determination, re-heating test, crushing strength and modulus of rupture tests. Many of these, including the chemical analysis, softening point test, load test and others of a like nature, need not be repeated unless in exceptional cases. However, the specific-gravity test, checked by the expansion test, will always indicate the conditions of the burn. The modulus of rupture will indicate the strength of the material. These last three tests, when used for purposes of control, are deemed sufficient for that purpose.

It is very interesting to note the temperatures at which the silica brick tested by the authors softened. In reporting the results one factor has been overlooked. The fact that a silica brick, when heated throughout, softens at 2900° F. does not mean that it cannot be heated in use at 3000° F. or 3100° F. The factor of heat conductivity has been overlooked. We have softened cone 33 in a furnace made of material softening at cone 32. This furnace was thin walled and its conductivity was high. Such a furnace, made from cone 32 material, gives good service at cone 32 and cone 33. A similar case is found in the malleable furnace and many others in which the silica bricks are often subjected to temperatures higher than their softening points. (Revised schedule of cone softening temperatures.)

This state of affairs is more true of silica brick than of fire-clay brick. At very high temperatures, the conductivity of silica brick is such that, although they may soften at 2900° F. when heated throughout, they give good service above 3000° F. if not over-insulated. A thin "glaze" forms on the hot portion of the brick but extends only for a short distance into the brick. The portions not immediately in contact with the hot zone are so protected that their softening temperature is not even approached, while the hot portion is so very viscous that it is not deformed.

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D. W. ROSS: The authors of this paper have indicated the importance of familiarity with the raw material from which a silica brick is made—when determining the nature of the brick

and its value for any given purpose. This point is worthy of serious attention.

The nature of the work which these authors have been doing has involved the testing of large numbers of silica brick and in this connection they have applied the specific-gravity test, mentioned in their paper, to brick made from quite a variety of raw materials. It is gratifying to the writer that they report favorably on this test. However, I am inclined to place more confidence in the results of specific-gravity tests in which the test pieces have been subjected to a vacuum (equivalent to 24" of mercury) while immersed in hot water rather than in those in which the test pieces have been merely boiled in water. It would also appear advisable to use test pieces of a size such that determinations upon them will represent the average properties of the brick, thus avoiding the possibility of merely obtaining the properties of a few abnormal particles.

Before recommending or condemning a brick on its softening temperature, it would appear necessary to know the nature of the raw material.

In a determination of the bonding strength, the cross breaking test on silica brick placed on edge (6" between supports) appears preferable to the compression test. Silica brick apparently fail in this test through a tearing apart of the material below the neutral axis rather than by the crushing of that above it. If, perchance, a brick fails by shearing over one of the knife edges, this can easily be detected and the results on that particular specimen may be eliminated.

R. J. MONTGOMERY: Mr. Klein's statement, as to establishing the expansion of the brick upon burning, is correct and is referred to by the authors in the statement "under-burning may be detected by linear measurements and tapping with a hammer." The quality of any silica brick that does not have a good ring is open to question and this is a good plant test—even though it does not always detect under-burned brick. A brick having a poor ring is apt to be under-burned or lacking in bond.

Mr. Howe and Mr. Ross question the method used in making

the specific-gravity determination. M. F. Beecher¹ reports considerable work on the various methods of obtaining saturation and concludes that "Saturation by boiling in water for 45 minutes to one hour is sufficient for the absorption determination," when tests are being made on the same kind of materials for comparison, and that the "treatment with a vacuum does not offer better results." The above confirms the experience of the authors. As to the size of the test pieces, used in making the specific-gravity tests, correct results may be secured from 20-gram samples providing that the results on two samples, taken from different parts of a brick, check each other.

Specific-gravity determinations on four brick, from different plants and varying quite widely in the degree of burning, gave the following results:

Sample.	Trial No.	2" cube. Sp. gr.	1 1/4" cube. Sp. gr.	3/4" cube. Sp. gr.	1/2" cube. Sp. gr.
2328	1	2.43	2.43	2.44	2.41
	2	2.40	2.43	2.44	2.42
2150	1	2.27	2.29	2.30	2.28
	2	2.27	2.28	2.30	2.28
1995	1	2.47	2.48	2.51	2.48
	2	2.49	2.49	2.49	2.48
1997	1	2.31	2.33	2.34	2.32
	2	2.30	2.33	2.33	2.32

In making the above tests, cubes varying from 2" to 1/2" were taken from each brick and subjected to the following boiling treatment:

- 2" cubes weighing about 260 g. were boiled 4 hours
- 1 3/4" cubes weighing about 65 g. were boiled 3 hours
- 3/4" cubes weighing about 18 g. were boiled 2 hours
- 1/2" cubes weighing about 10 g. were boiled 1 hour

The above results indicate that if the specific-gravity determination is made on a 2" cube, boiling will not give complete saturation—as the higher values were obtained with the smaller cubes. A piece weighing from 18 to 65 grams gave the best results. The results on a 10-gram piece are not as reliable as those secured on

¹ *Trans. Am. Ceram. Soc.*, 18, p. 73.

the medium-sized pieces but check more closely than do those on the 260-gram pieces.

Mr. Howe's reference to flame temperatures, as high as 3000° F., reached in furnaces constructed of silica brick, brings out an important truth which has lead to the steatment by many manufacturers and users that a silica brick will actually withstand temperatures above its softening point.

The re-burning test, noted by Mr. Howe, is referred to in the paper under the paragraph on specific gravity—some results obtained by this test being tabulated.

POLYCHROME DECORATION OF TERRA COTTA WITH SOLUBLE METALLIC SALTS.

By HEWITT WILSON, Columbus, Ohio.

The terra cotta manufacturer is looking for some cheap, quick and easy way of applying two or more colors to the same piece of ware. He does not have to be as particular as the potter in the nicety of the lines and the delicacy of the colors. Most of his work is placed beyond the range of close inspection and his colored areas are comparatively large.

The method of polychroming best suited to any given order of terra cotta must be determined from (a) the size of the colored areas, (b) the number of colors or colored areas on the same piece, (c) the shape and finish of the outline of the colored areas, and (d) the respective colors to be applied. Often a combination of several methods is necessary before the order is completed.

The present methods of applying colors are:

(1) **Painting Colored Glazes onto the Required Areas with a Brush.**—This method is slow, expensive, and is liable to show streaking due to the variation in thickness of the glaze. A great many glazes of the Bristol type or variations of the same cannot be painted without developing cracks on drying caused by the unevenness of the coating—these cracks do not heal in the kiln. This method finds the greatest usefulness with glazes of low viscosity—which flow and cover well and which are usually burned to the lower temperatures. It is more adapted to small areas and small ornamental features than to large ones.

(2) **Spraying the Colored Glazes with Masques.**—By this method a paper, plaster or metal covering is placed on the part not to be coated at that time and the exposed portion is sprayed. The placing and shifting of the masques injures the freshly sprayed surfaces and leaves uneven and broken lines between adjoining colors. This is a good method for large polychrome surfaces

and features in which the colors are arranged in simple repeating design.

(3) **Overglaze Spraying.**—In the first two methods, colored glazes are placed in their respective positions. By the third method a single glaze may be sprayed over the whole piece and the overglaze colorant sprayed with a fine spray onto the desired part and brushed off the other parts. It is difficult, without the use of shields, to apply more than one color in this manner to the same piece. It works well with small, complicated designs and over large areas.¹

(4) **Painting with Soluble Metallic Salts.**—This method was probably adopted from the underglaze decorative process—used for pottery and fine ware. In this process, soluble metallic salts are dissolved in glycerine and painted onto the biscuit or dry piece, dried to 120° C in order to set the glycerine, and fired to 800° C. The glaze is then applied and the piece burned to the proper maturing temperature.

Purdy² gives the following formulas for soluble underglaze colors:

		Grams.
Turquoise:	Cupric nitrate.....	50
	Glycerine.....	200
	Water.....	80
Light blue:	Cobalt nitrate.....	65
	Glycerine.....	115
	Water.....	50
Yellow:	Uranic nitrate.....	65
	Glycerine.....	60
	Water.....	40
Yellowish brown:	Ferric chloride.....	75
	Glycerine.....	75
	Water.....	50
Chamois:	Nickel nitrate.....	100
	Glycerine.....	100
	Water.....	100

¹ *Trans. Am. Ceram. Soc.*, **19**, 653 (1917).

² "Class Notes" (1912).

		Grams.
Gray:	Cobaltic nitrate.....	30
	Ferric chloride.....	10
	Glycerine.....	160
	Water.....	40
Green:	Chromic acid.....	100
	Water.....	100

For coloring terra cotta by this method, the piece is sprayed with a single glaze and the various solutions are painted onto the required areas. As the liquid quickly soaks into the dry glaze, no heating is required to set the glycerine. The ware is burned in the usual way in a single fire.

Mediums.—When water is used, save with cobalt sulphate and chromium acetate, the brush marks are too pronounced after firing. These two colorants spread easily and give uniform colors.

Glycerine is not absorbed by the dry glaze as quickly as water and allows the successive brushings to mingle. Alcohol may be used for thinning the solution. Many of the salt solutions are lacking in color so that the operator cannot detect the ground that has been covered. Common bluing or soluble dyes cause the painted areas to show distinctly.

Experimental.

Preparation.—The salts were weighed and ground together in a mortar. The required amounts of glycerine and alcohol were added and the whole ground until the salts had dissolved. The color was then applied on the dry glaze. If allowed to stand in the open, the concentration of the solutions is increased by evaporation and more coloring material will be added to the same area of base glaze with the same brush stroke. A less volatile medium than alcohol would be preferable for this reason. Many of the salts, for example some of the chlorides and sulphates, attack the carbonates in the glaze and cause bubbles and blisters. The nitrates and acetates are usually non-active in this respect.

Firing of Glazes and Colors.—After painting, the decorated trials were set, with no special precautions, in an ordinary terra cotta kiln and fired with the regular ware to cone 6-7. The glazes and underslip used were as follows:

GLAZES.				
Glaze "A".....	0.268 K ₂ O	}	0.417 Al ₂ O ₃	{ 2.138 SiO ₂
	0.468 CaO			
	0.264 ZnO			
Glaze "B".....	0.286 K ₂ O	}	0.446 Al ₂ O ₃	{ 2.331 SiO ₂
	0.403 CaO			
	0.146 ZnO			
	0.074 MgO			
	0.091 BaO			
Glaze "C".....	0.238 K ₂ O	}	0.430 Al ₂ O ₃	{ 2.902 SiO ₂
	0.354 CaO			
	0.210 ZnO			
	0.055 MgO			
	0.143 BaO			

VITREOUS SLIP.¹

Standard "K".

Flint.....	194
Cornwall-stone.....	437
China clay.....	242
Ball clay.....	117
	—
	990

"A" SERIES.

	1.	2.	3.	4.	5.	6.	7.	8.	9.
Cobalt sulphate.....	1.0	2.0	5.0	5.0	7.5	10.0	15.0	20.0	25.0 grams.
Water.....	100.0	100.0	100.0	50.0	50.0	50.0	50.0	50.0	50.0 cc.

Glaze "A".—The colors developed varied from light blue to dark blue. Very even colors can be produced by the use of water alone although glycerine aids in the ease of painting and insures uniformity.

Glaze "C".—This produced grayer blues than those of Glaze "A", although the range of colors is the same.

[illegible]

Glaze "A."—(1,2,3) Blue-greens. (4,5) Good greens. (6,7,8) Yellow-greens. (9) Brown-green.

Glaze "B."—(1,2,3) Best greens. The remainder of the series are yellow and yellow-brown-greens. All are good.

Glaze "C."—(1,2) Gray-blue. (3,4) Green-gray. (5,6) Green-brown. (7,8,9) Dark green-brown.

Standard Slip "K."—Blues to gray-browns. (5,6,7) Have a slight green tinge. (3) Was flashed and a blue-black.

"F" SERIES.

	1.	2.	3.	4.	5.
Antimony chloride.....	10.0	10.0	10.0	10.0	10.0 Cc.
Rutile.....	0.0	0.5	1.0	1.5	2.0 Grams
Glycerine.....	10.0	10.0	10.0	10.0	10.0 Cc.
Soda ash.....	6.0	6.0	6.0	6.0	6.0 Grams

Glaze "A."—(1,2) Gray. (3,4,5) Yellow scummed.

Glaze "B."—(1) No color, scummed surface. (2) Faint orange tinge. (3) Spotted orange. (4) Orange but variable. (5) Crawled, variable rutile orange.

Glaze "C."—(1,2) Light gray. (3,4,5) Best yellows of all glazes. The acid in the antimony chloride attacks the carbonates of the glazes and causes blistering. Hence the soda ash was added to neutralize the acid without success.

Standard "K."—Yellow with good increase of orange colors with the series. Blistering.

"G" SERIES.

	1.	2.	3.	4.	5.
Cobalt sulphate.....	1.0	1.0	1.0	1.0	1.0 Grams
Uranium nitrate.....	6.0	6.0	6.0	6.0	6.0 Grams
Iron chloride.....	0.0	1.0	2.0	4.0	8.0 Grams
Alcohol.....	10.0	10.0	10.0	10.0	10.0 Cc.
Glycerine.....	10.0	10.0	10.0	10.0	10.0 Cc.

Glaze "A."—(1,2) Good greens. (3,4,5) Give lighter and browner colors.

Glaze "B."—(1) Dark almost black-green. (5) Yellow-brown-green. Good even colors.

Glaze "C."—Dark gray-greens to greenish browns. The iron affords an individual brown color in spots.

Standard "K."—(1) Gray-black to light neutral gray. (5) Iron acts as a diluent and does not intensify the color.

"H" SERIES.

	1.	2.	3.	4.	5.
Cobalt sulphate.....	1.0	1.0	1.0	1.0	1.0 Grams
Uranium nitrate.....	6.0	6.0	6.0	6.0	6.0 Grams
Iron chloride.....	2.0	2.0	2.0	2.0	2.0 Grams
Chromium acetate.....	0.0	0.5	1.0	2.0	4.0 Grams
Alcohol.....	10.0	15.0	15.0	15.0	15.0 Cc.
Glycerine.....	10.0	10.0	10.0	10.0	10.0 Cc.

Glaze "A."—(1,2) Uranium greens. (3,4,5) Green-browns.

Glaze "B."—(1,2) Yellow-green. (3,4) Yellow-brown. (5) Buff-brown.

Glaze "C."—(1) Gray-green. (2) Brown-green. (3,4,5) Browns.

Standard "K."—(1) Dark blue-gray. (2,3,4,5) Grays and blacks.

"I" SERIES.

	1.	2.	3.	4.	5.
Uranium nitrate.....	4.0	2.0	1.0	0.5	0.0 Grams
Iron chloride.....	0.0	0.5	1.0	2.0	4.0 Grams
Alcohol.....	10.0	10.0	10.0	10.0	10.0 Cc.
Glycerine.....	10.0	10.0	10.0	10.0	10.0 Cc.

Glaze "A."—(1,2) Varying uranium greens. (3) Light yellow. (4,5) Light buffs.

Glaze "B."—(1,2) More orange than Glaze "A." (3) Bright yellow. (4,5) Light buffs.

Glaze "C."—(1,2) Yellow and brown-green. (3) Light buff-yellow. (4,5) Brown edged yellow-buffs.

Standard "K."—(1,2) Blue-grays. (3,4) Light buffs. (5) Good tan.

"J" SERIES.

	1.	2.	3.	4.	5.
Tin chloride.....	5.0	10.0	15.0	20.0	25.0 Grams
Chromium acetate saturated in alcohol	0.0	5.0	5.0	5.0	5.0 Cc.
Glycerine.....	10.0	10.0	10.0	10.0	10.0 Cc.
Alcohol.....	5.0	7.5	15.0	20.0	25.0 Cc.

Glazes "B" and "C."—Pink colors but crowfooted, dry and blistered. Some of the blistering occurs in the application. "K" series is good with (4) of "J" series.

"K" SERIES.

	1.	2.	3.	4.	5.	
Tin chloride.....	20.0	20.0	20.0	20.0	20.0	Grams
Chromium acetate saturated in alcohol	0.0	2.0	4.0	8.0	16.0	Cc.
Glycerine.....	10.0	10.0	10.0	10.0	10.0	Cc.
Alcohol.....	25.0	23.0	21.0	17.0	9.0	Cc.

Glaze "B."—(1) Light pink but crowfooted. (2-5) Increasing pinkness. Very good colors.

Glaze "C."—(1,2) Light pinks, dry glaze. (3,4,5) Increasing pinkness but with a buff tinge.

"L" SERIES.

	1.	2.	3.	4.	5.	
Tin chloride.....	20.0	20.0	20.0	20.0	20.0	Grams
Chromium acetate (5 per cent. in H ₂ O).	2.0	4.0	8.0	16.0	25.0	Cc.
Alcohol.....	8.0	6.0	2.0	0.0	0.0	Cc.
Glycerine.....	10.0	10.0	10.0	10.0	10.0	Cc.

Glaze "B."—Pink colors are good and equal to those of "K" series.

Glaze "C."—(1,2) Light pink, liable to crowfoot, blister and be dry. (3,4,5) Very light pink, lighter than "K" series.

"M" SERIES.

	1.	2.	3.	4.	5.	
Manganese sulphate.....	5.0	10.0	15.0	20.0	25.0	Grams
Alcohol.....	5.0	10.0	10.0	10.0	10.0	Cc.
Glycerine.....	10.0	10.0	10.0	10.0	10.0	Cc.

Standard "K."—(1) Light gray. (2) Dark brown glazed surface. (3-5) Increasing dark brown variegated colors which can be used if the running of the glaze is allowed for. Manganese lowers the viscosity considerably.

Glazes "B" and "C."—(1) Medium brown to streaked browns and blacks in (3,4,5). Manganese sulphate melts into a glaze by itself, whether in standard or glaze.

"N" SERIES.

	1.	2.	3.	4.	5.
Potassium permanganate.....	5.0	10.0	15.0	20.0	25.0 Grams
Alcohol.....	5.0	10.0	10.0	16.0	25.0 Cc.
Glycerine.....	10.0	10.0	15.0	18.0	18.0 Cc.

These mixtures become warm with emission of a white vapor and bubble when mixed with alcohol. This does not work as well as the sulphate, showing blistering, peeling and dryness. Colors are not even and brush marks show.

"O" SERIES.

	1.	2.	3.	4.	5.
Potassium permanganate.....	0.0	0.5	1.0	1.5	2.0 Grams
Cobalt sulphate.....	1.0	1.0	1.0	1.0	1.0 Grams
Iron chloride.....	6.0	6.0	6.0	6.0	6.0 Grams
Chromium acetate.....	0.5	1.0	1.5	2.0	2.5 Grams
Glycerine.....	10.0	10.0	12.0	15.0	15.0 Cc.
Alcohol.....	5.0	5.0	7.5	10.0	10.0 Cc.

Glaze "B."—Light and darker mottled brown-grays to a dark brown.

Glaze "C."—Good red-browns, the color varying with the painting.

Standard "K."—(1) Gray. (2,3,4,5) are dark browns and blacks.

"P" SERIES.

	1.	2.	3.	4.	5.
Cobalt sulphate.....	5.0	3.0	1.0	1.0	1.0 Grams
Iron chloride.....	6.0	6.0	6.0	8.0	10.0 Grams
Glycerine.....	10.0	10.0	10.0	10.0	10.0 Cc.
Alcohol.....	10.0	10.0	10.0	10.0	10.0 Cc.

Glaze "B."—(1,2) Violet-blues. (3) Light blue-gray. (4,5) Buff, blue.

Glaze "C."—(1,2) Gray-blues. (3,4,5) Light blue-grays.

Standard "K."—(1) Flashed, blue-gray. (2) Dark green-black flashed. (3,4,5) Good browns.

"Q" SERIES.

	1.	2.	3.	4.	5.
Rutile.....	0.2	0.5	1.0	2.0	4.0 Grams
Glycerine.....	10.0	10.0	10.0	10.0	10.0 Cc.

Glaze "B."—(1,2) Faint streaks of yellow. (3) Darker and streaked.

Glaze "C."—(4,5) Rutile yellow-brown, badly wrinkled.

Standard "K."—Good even colors ranging from light brown to red-brown. May be used. As the rutile did not dissolve, this was an overglaze decoration rather than a soluble stain.

"R" SERIES.

	1.	2.	3.	4.	5.
Iron chloride.....	2.0	4.0	8.0	16.0	25.0 Grams
Alcohol.....	10.0	10.0	10.0	10.0	10.0 Cc.
Glycerine.....	10.0	10.0	10.0	10.0	10.0 Cc.

Glaze "B."—(1,2) Very light yellow. (3) Light brown. (4,5) Dark-red-brown.

Glaze "C."—(1,2) Light buffs. (3,4,5) Increasing red-browns.

Standard "K."—(1,2,3) Light gray-buffs. (4,5) Red-browns, varying.

All are good colors but vary as the iron volatilizes in burning.

"S" SERIES.

	1.	2.	3.	4.	5.
Copper sulphate.....	2.0	4.0	8.0	16.0	25.0 Grams
Alcohol.....	10.0	10.0	10.0	10.0	10.0 Cc.
Glycerine.....	10.0	10.0	10.0	10.0	10.0 Cc.

Glaze "B."—Colors duplicate those of glaze "C" but show more black and not too much good green. This is just the reverse of the uranium series in which Glaze "C" gives the poor greens.

Glaze "C."—(1) Light copper-green, good and uniform. (2) Varying copper-green, fair. (3,4,5) Green-blacks and black. No defects.

Standard "K."—(1,2) Just faintly off color. (3) Light greenish shades, blistered. (4,5) Uniform black.

"T" SERIES.

	1.	2.	3.	4.	5.
Nickel sulphate.....	2.0	4.0	8.0	16.0	25.0 Grams
Alcohol.....	10.0	10.0	10.0	10.0	10.0 Cc.
Glycerine.....	10.0	10.0	10.0	10.0	10.0 Cc.

Glaze "B."—(1) Good nickel-purple, uniform. (2) Lighter than (1). (3) Purplish gray. (4,5) Peeled and showing unmelted green dust which rubs off easily.

Glaze "C."—(1,3) Good browns, uniform. (4,5) Unmelted, rub off.

Standard "K."—Good browns. (4,5) Greenish unmelted dust.

From the above series, the best colors were selected and used in painting ornamental terra cotta, including bits of scenery.

An unskilled man, not used to handling a brush, did very good work after a few days' practice.

RESULTS.

Colors with the Glazes.

Blue.—Good blues are very easily produced with cobalt sulphate in all of the glazes. Varying the amount of the sulphate from 0.5 g. to 30.0 g. per 100 cc. of water will give a range from a very light sky-blue to the ordinary deep blue. Beyond this amount the color darkens rapidly to blue-blacks.

Green.—Because of the zinc used in the glazes of this study, chromium salts gave tans and browns which are stable, uniform, and easy to use. However, the green from chromium in zincless glazes was not good and could not be relied upon.

The best green colors were produced from the uranium-cobalt combination in the mat glazes "A" and "B". The gloss glaze "C" gave gray-greens. The best proportions were uranium nitrate 6 grams, cobalt sulphate 1.0 to 3.0 grams, alcohol 10 cc. and glycerine 10 cc.

The copper-greens were variable and faded. However, Glaze "C", which gave poor greens with cobalt and uranium, gave better results with the copper.

Pink.—Uniform light pink colors can be produced in the above glazes with mixtures of tin chloride and chromium acetate. 20 grams of tin chloride, 16 cc. of a saturated solution of chromium acetate in alcohol, with 10 cc. of glycerine and 9 cc. of alcohol, gave good light pinks.

Browns.—Manganese sulphate 10 g., alcohol 10 cc. and glycerine 10 cc. gave fair browns. If made stronger than this or if painted heavily, it will darken from brown to black and run when applied on an inclined surface. If more dilute the manganese will produce good grays. These browns, grays and blacks may be varied by blending with cobalt, iron and chromium as in the "O" series.

Nickel Sulphate with Glazes "A" and "B" produced light purple and gray colors¹ but with Glaze "C" it gave good uniform browns.

Chromium Acetate in a glaze containing zinc gives good uniform tans and browns.

Iron Chloride gave red-browns but these were variable at the firing temperature.

Yellow.—Dilute uranium sulphate or nitrate alone or with iron chloride gave promise of fair light yellow shades. However, when tried out further they were not very reliable.

Gray.—This may be produced from several sources depending on the shade desired. Blue-grays were obtained in Glaze "C" with cobalt and uranium—the uranium content being lower and the cobalt higher than used for the production of green colors. (See Series "D.")

Violet.—Cobalt and iron in "P" series gave violet and blue-grays with a ratio of cobalt sulphate to iron chloride varying from 5 : 6 to 1 : 10, respectively. Dilute manganese gives brownish grays.

Colors with Vitreous Slip "K."

Blues are easily obtained with cobalt sulphate. Most of the other salts or combinations give grays, browns or blacks. The colors are not as bright as those developed in the glazes.

Browns.—Dilute uranium gave gray, strong uranium gave gray-browns.

Uranium and cobalt combinations gave blue and green-blacks.

Iron gives buffs and red-browns.

Manganese gives grays, browns and blacks, of different shades, however, than those produced in the glazes.

¹ *Trans. Am. Ceram. Soc.*, **14**, 141 (1912).

Rutile painted on the surface with glycerine gives good light buffs and buff-browns.

Copper sulphate gives light green-grays running into blacks.

Nickel gave good browns.

In conclusion, we wish to state that the Denver Terra Cotta Company has also used this method on shop orders with success and in fact is the pioneer for this method of color decoration of terra cotta on a large scale.

OHIO STATE UNIVERSITY.

DISCUSSION.

MR. BURT: I would like to ask Mr. Wilson if he has not experienced large variations in color when using the glazes containing the soluble salts. In other words—does not the personal factor influence the depth of color secured by spraying with the brush?

MR. WILSON: The amount of solution on the brush, the speed of the brush across the absorbent surface of the dry glaze and the repeated number of strokes over the same surface, all have an influence on the amount of coloring material added to a given square inch of glaze surface.

If the concentration of the solution is so made that a moderate soaking action of the glaze surface is necessary to produce the desired depth of color, more uniform results can be expected both in regard to the shade and to the elimination of the brush markings. This aids in the solution of the personal factor problem.

MR. TRUMAN: I should like to ask Mr. Wilson if, in weighing out the soluble salts, he did not experience some difficulties through their absorption of moisture from the atmosphere? I have experienced this difficulty in weighing out chloride of iron.

MR. WILSON: Some of the salts absorb moisture very rapidly. They must be weighed very quickly.

MR. TRUMAN: In some of my work in which soluble salts were used, I found it advantageous to add the salts in the form of saturated solutions of predetermined specific gravity.

MR. MINTON: I would ask Mr. Wilson whether he has determined the relative behavior of cobalt borate and cobalt sulphate in his glaze work? I understand that the cobalt borate is to be preferred.

MR. WILSON: I have encountered some blistering of the glazes when using chromium sulphate. I did not experience this difficulty when using cobalt sulphate. I can see no objection to the use of cobalt borate although I have not used it.

MR. RADCLIFFE: My experience has been similar to that of Mr. Truman's in regard to the variation in color, and I have found that the best method was to use solutions of the soluble salts, controlling their specific gravities by means of a hygrometer. In this way the variation in color was reduced to a minimum. Some of these soluble salts do cause blistering of the glazes during their application—due to the acid in the salts. This difficulty may be overcome by the addition of a metallic oxide to the solution and neutralizing the acid.

JOURNAL OF THE AMERICAN CERAMIC SOCIETY

A monthly journal devoted to the arts and sciences related to the silicate industries.

Vol. 1

June, 1918

No. 6

EDITORIALS.

CLAY PRODUCTS AT THE CHEMICAL EXPOSITION.¹

A survey of the exhibits at the Grand Central Palace revealed the fact that while many products of the ceramic industries, other than glass, are indispensable in the processes of chemical manufacture and research, the exhibits of these were not very numerous. There were found at the Exposition three displays of chemical porcelain, two of chemical stoneware, one of fire brick, three of laboratory refractories, one of insulating material, one of vitrified cells for acid towers, and two of enameled iron.

Chemical Porcelain.

The exhibits of chemical porcelain were those of the Coors Porcelain Company, the Guernsey Earthenware Company, and the Ohio Pottery Company. Inasmuch as no criterion for chemical porcelain can be advanced without the evidence afforded by special tests, it is not possible in a review such as this to make any mention of quality. It will suffice, therefore, to describe the three exhibits as one, especially as the same excellence in manufacture and resource is evident in each case. The improvements effected since the Exposition of last year were quite marked. All the factories are now successfully producing evap-

¹ Fourth National Exposition of Chemical Industries, Grand Central Palace, week of September 23, 1918. Reference to the Chemical Exposition in the June number of THIS JOURNAL is accounted for by the fact that the January number of Vol. 1 of the JOURNAL was issued in July of this year—the succeeding numbers being correspondingly late.

orating dishes, both flat and curved, of twenty-inch diameter, while of course the usual laboratory sizes of these, together with beakers, crucibles, casseroles and spatulas, were strongly in evidence. The mastery of the technical difficulties in the workshop is well shown by the excellent production of delicate porcelain plates with minute perforations. Some of these form the bottoms of Gooch crucibles, while others are detached. Certainly no finer specimens of workmanship are made anywhere.

Chemical Stoneware.

The two exhibits of chemical stoneware may likewise be considered together. They were by the General Ceramics Company, of Keasbey, New Jersey, and Maurice A. Knight, of East Akron, Ohio. The modern chemical stoneware is thoroughly vitrified throughout. It is said that the glaze is added for appearance only, but the smooth polished surfaces of pump plungers and valve balls is satisfactory both to the sight and touch. The structural intricacy of some of the pieces is a marvel to any observer, but to those who are versed in the especial difficulties of clay-shaping and firing, it is a veritable miracle. No problem of construction seems to baffle these potters; huge tanks and jars which would drown a goodly proportion of the Forty Thieves, condensing worms larger than any barrel, valves, spigots, traps, siphons in great variety, and all of them perfect, sonorous and acid-proof pottery. Certainly there is no need for imported wares in this department of ceramics.

The exhibit of vitrified packing for acid towers seemed to be something new. The B. Mifflin Hood Company, of Atlanta, Georgia, have produced, apparently from an auger die, a tube about two inches in diameter which contains a spiral coil. The ingenuity of the product itself is quite fascinating and, given a burned clay perfectly resistant to the acid, the piece would seem to be ideal for its purpose. A large exposed surface is combined with a minimum weight.

Refractories.

The only exhibit of fire brick was that of the Didier-March Company of Keasbey, N. J. The wares, so far as inspection might

warrant, were of excellent quality and the only regret is that other manufacturers did not exhibit. Fire brick are not, of course, an accessory special to chemical manufacture and yet, in these days of high temperatures, chemists have a very real interest in the quality of refractories.

Of more direct interest were the displays of laboratory refractories by the Carborundum Company, of Niagara Falls, New York, the Denver Fire Clay Company, of Denver, Colorado, and the Norton Company, of Worcester, Massachusetts. The first named showed especially the larger pieces, such as muffles and crucibles of carborundum bonded with clay. The Denver Fire Clay Company had an excellent display of fire clay crucibles of all sizes, and a complete line of cupels and scorifiers. The Norton Company specialized in the smaller wares, some of which were intricate in form and all were well made—crucibles and boats for analytical work, tubes for electric furnaces and pyrometers, as well as small cones and thimbles for special operations.

The Sil-O-Cel Company showed a collection of insulating material with which an interesting and effective exhibit was made. Several illustrative units were shown in which the insulating properties of the material were compared with those of fire brick and other standard materials.

THE GLASSWARE EXHIBITS AT THE EXPOSITION.

Among the ceramic exhibits, those of glassware proved to be of high interest. Since the exhibition was limited to products of direct relation to the chemical industries, the glassware exhibits represented a very small field of the entire glass industry, but this field is one of the greatest importance to the chemical industries and to those industries in which chemists and chemical laboratories are essential.

The glassware exhibits comprised three groups, namely, exhibits by glass manufacturers; exhibits by apparatus dealers, by whom the bulk of the special apparatus is made before the lamp; and exhibits by manufacturers of fused silica.

Of the glass manufacturers, the exhibit of the Corning Glass Company was the largest and most elaborate. A variety of "Pyrex" laboratory apparatus and baking dishes formed the

basis of the display. In addition, there were exhibits of "Frensel" lenses and other signaling lights in a variety of colors as well as of lenses for automobile and other headlights. One of the features of this exhibit was the glass tubing for special purposes. In this was included tubing for burettes and "lens" tubing especially for clinical thermometers. Demonstration was also made of a lamp equipped with daylight glass. Popular attention was attracted by a glass blower who demonstrated the simplicity of working glass before the lamp.

The booth of the Macbeth-Evans Glass Company was devoted to an exhibit of their well-known laboratory glassware. The exhibit was simple, well chosen, and displayed the usual excellent workmanship. One feature of the exhibit was a twenty-inch "balloon flask" (18 gallons), used in mixing fulminate compositions.

One exhibit of the Whitall Tatum Glass Co. consisted of a simple display of the long and favorably known "non sol" chemical laboratory apparatus, together with a selection of reagent bottles in a variety of forms.

Of the dealers' exhibits, that of the Emil Greiner Co. was of commanding interest. It might almost be characterized by "anything with a glass stopcock." This was not, however, the limit of the exhibit. Thermometers, intricate absorption apparatus, condensers, fractionating columns and Dewar flasks, were features.

The glass exhibit of the Central Scientific Co. comprised only a small portion of their total display. One exhibit was of interest, however, in view of the standardization of sizes and shapes of laboratory apparatus and the construction of special apparatus in accordance with the specifications of American scientists.

An industry comparatively new to America is the production of fused silica and quartz glass. The former, the opaque product, and the latter, the transparent variety, were exhibited by the Sidio Co. of America and by the Hanovia Chemical and Manufacturing Co., respectively. Although these exhibits were limited to small- and medium-sized apparatus, the excellence of workmanship indicates that real progress is being made in this new and important industry.

The Thermal Syndicate also presented an exhibit of their well-known products. This exhibit was characterized by a display of the larger sized apparatus. The features were a nitric acid condensing system, of elaborate construction, and a display of drawn tubing in ten-foot lengths and ranging up to four inches in diameter. A line of the smaller articles in transparent silica has recently been added.

Akin to the exhibits of glassware were those of enameled iron apparatus displayed by the Elyria Enameled Products Co. and by the Pfaudler Co. These exhibits deserve more than the passing mention here given them, for they represent real progress in an important field of ceramics.

The glass exhibits, as a whole, were pleasing and were creditable to the American industries. It is to be regretted that a larger number of manufacturers of glass apparatus were not represented, but the exhibits demonstrate that the necessary technical knowledge is not wanting in this line. It is reassuring to observe that the principal handicap, the lack of manual and mechanical skill, is rapidly being overcome and that a permanent American industry in scientific glassware is being surely established.

AMERICAN CERAMIC SOCIETY EXHIBIT AT THE EXPOSITION.

BY C. H. KERR.

One of the features of the Ceramic Section of the Exposition was a series of eight charts displayed upon the walls of the American Ceramic Society's booth. The interest and comment which the charts aroused at the Exposition seemed to warrant their reproduction in the JOURNAL and they are therefore presented in this issue.

Very few, even of the members of the American Ceramic Society, have any clear conception of the great magnitude of the ceramic industries, either considered as separate branches of the industry, such as fire brick, pottery, glass, cement, etc., or considered in the aggregate, and it is not at all surprising, therefore, that the general chemist or the specialist in some other branch of applied science should be quite startled to learn that the value of ceramic products is about one-third greater than the value of electrical machinery, about two and a half times

the value of the potato crop of the Nation, and more than twice the value of the petroleum products of the country.

While the charts show the approximate figures, it may be of interest to record the values, in round numbers, from which the charts were prepared. The figures are the Government official figures, taken from the Census Reports for the year 1914. Later reports are available in many instances but the World War has created such havoc with industrial statistics that the older figures are considered more reliable in showing the relative proportions of the various industries.

For the Manufactured Products the figures used in Chart No. 1 were:

Cotton goods.....	\$701,000,000
Men's clothing.....	584,000,000
Chemical industries	548,000,000
Ceramic industries.....	447,000,000
Petroleum refining.....	396,000,000
Woolen goods.....	395,000,000
Electrical machinery	335,000,000
Blast furnace products.....	318,000,000

For Mineral Products the figures used in Chart No. 2 were:

Coal, soft.....	\$493,000,000
Ceramic products.....	447,000,000
Iron ore	299,000,000
Petroleum.....	214,000,000
Coal, hard.....	188,000,000
Copper.....	153,000,000
Gold.....	94,000,000
Silver.....	40,000,000

The statistics regarding Agricultural Products (Chart No. 3) are of the greatest interest, for, after all, the United States is chiefly an agricultural nation though we are very apt to overlook that fact because the agricultural production is made up of innumerable small units rather than large, segregated groups. We do not have a farm or a group of farms to compare with the United States Steel Corporation, but we do have the grand

totals of agricultural products that dwarf even our immense totals in manufactured products. The charts showing the relative value of Ceramic Products in comparison with agricultural Products is based upon the following figures:

Corn.....	\$1,722,000,000
Wheat.....	878,000,000
Hay.....	779,000,000
Cotton.....	720,000,000
Oats.....	499,000,000
Ceramic products.....	447,000,000
Potatoes.....	199,000,000
Tobacco.....	96,000,000

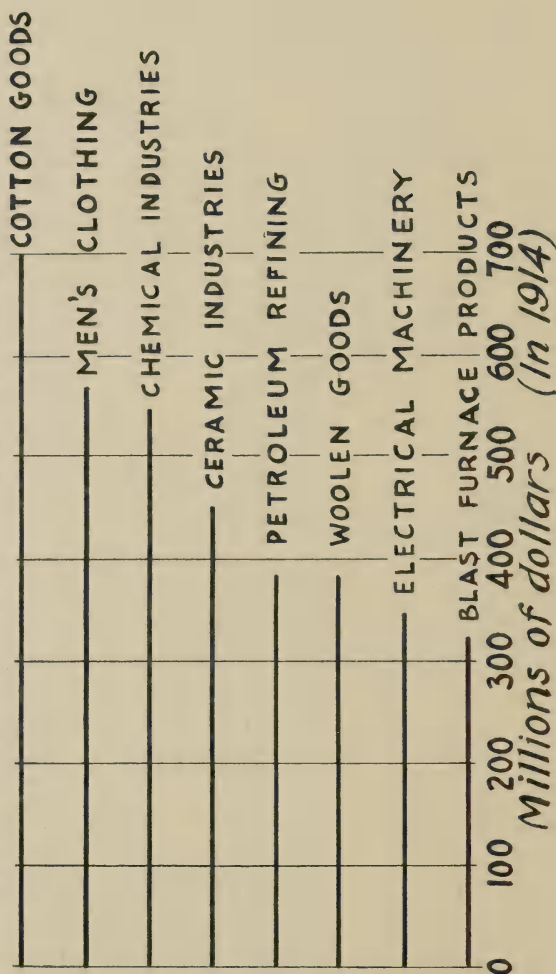
In all of the above statistics there are included in the ceramic industries the manufacture of clay wares of all kinds, glass, cement, enameled wares, plasters, lime, abrasive products and allied articles usually understood as being embraced within the ceramic field. To analyze the items, making up the impressive aggregate of 447 million dollars a year for the ceramic industries, would be very instructive and very surprising, but that must be left for a later issue of the JOURNAL.

The most interesting curve shown at the Society's booth was that which displayed in graphic form the growth of the American Ceramic Society (Chart No. 4). Founded in 1898 and starting its real existence in 1899, the membership shows a steady and consistent growth to somewhat over 500 in 1917. In 1918 the growth has been unusual and the membership has more than doubled. At the time of the Exposition the Society had about 1100 members enrolled. It is eminently fitting that the ceramic industry, one of the most ancient of all the manufacturing arts, should have as a clearing house for its scientific activities, an organization with the size and power of the American Ceramic Society.

Very few people, even among those engaged in ceramic work, realize the great number of ceramic products which involve the use of the various every-day raw materials, and still fewer appreciate how exceedingly vital the ceramic industry is today in supplying the products upon which other industries depend. These

MANUFACTURED PRODUCTS

THE VALUE OF CERAMIC PRODUCTS COMPARED WITH WELL KNOWN MANUFACTURED PRODUCTS



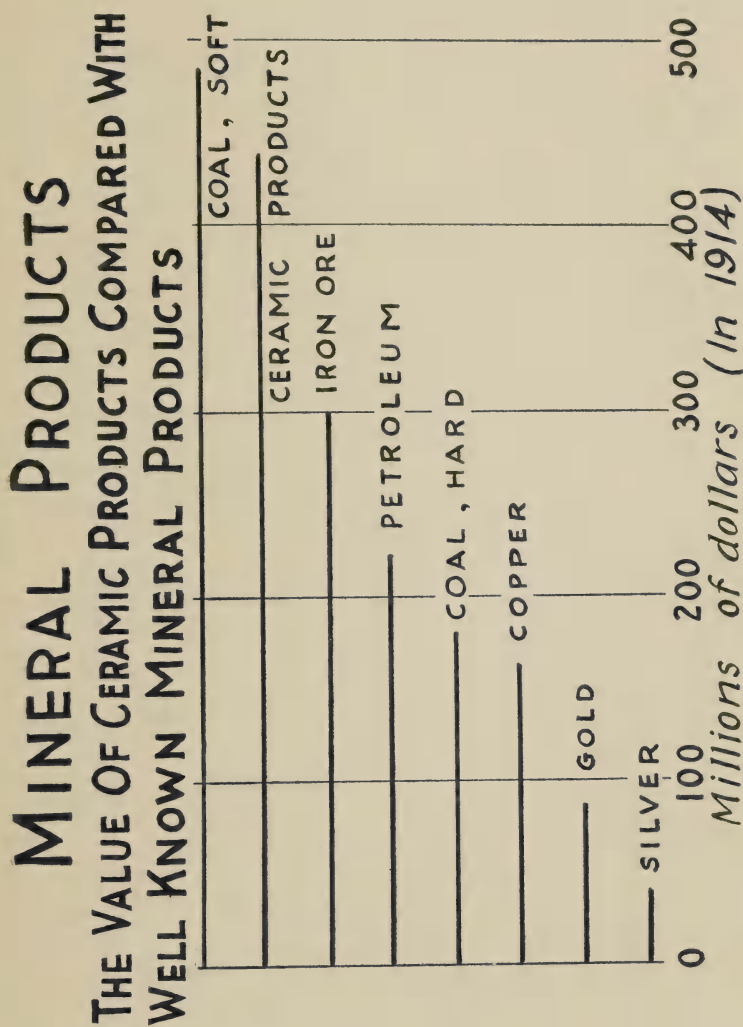


CHART No. 2.

AGRICULTURAL PRODUCTS

THE VALUE OF CERAMIC PRODUCTS COMPARED WITH WELL KNOWN AGRICULTURAL PRODUCTS

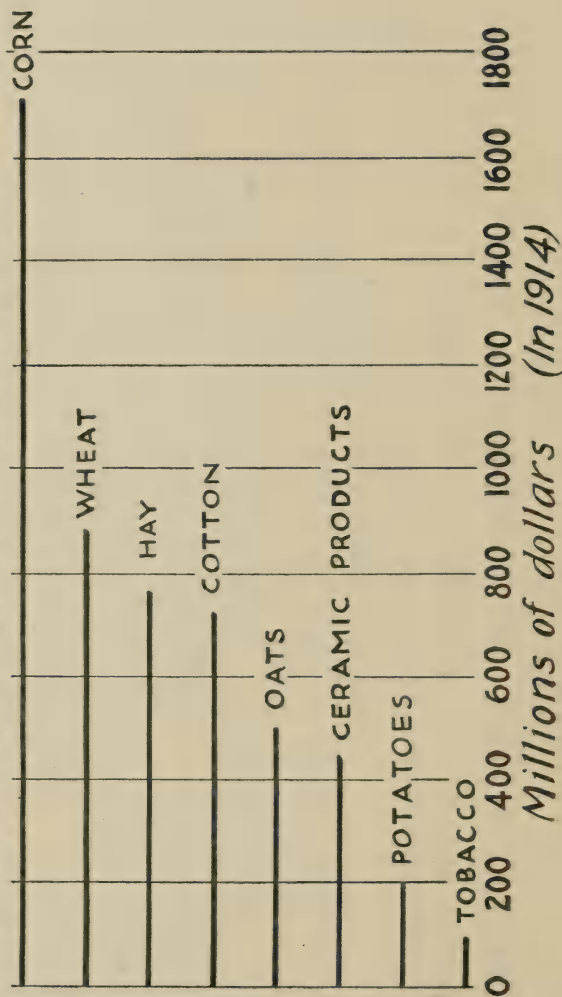


CHART No. 3.

MEMBERSHIP GROWTH

CURVE SHOWING AMERICAN CERAMIC SOCIETY'S
GROWTH SINCE ORGANIZATION IN 1899

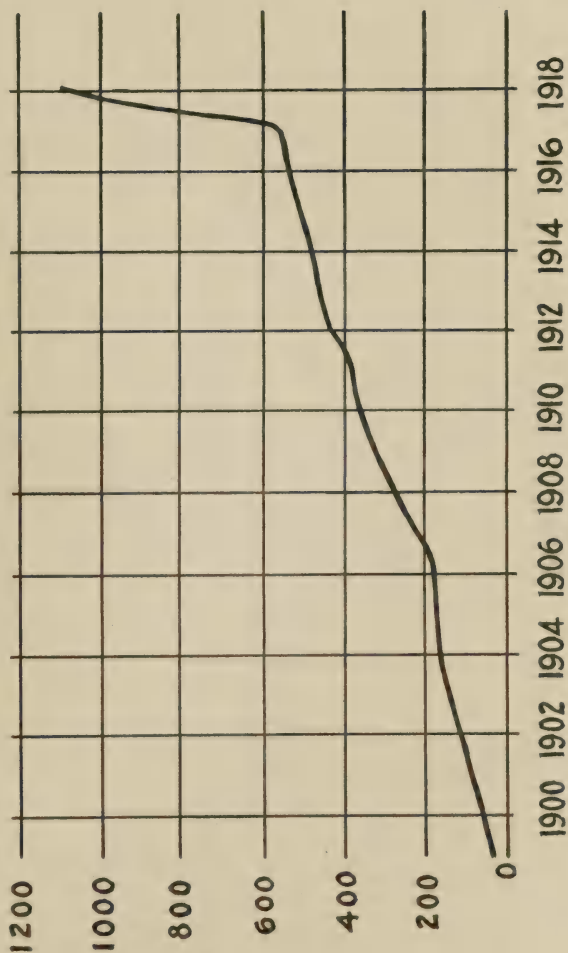


CHART No. 4.

RAW MATERIALS OF THE CERAMIC INDUSTRIES AND THE PRODUCTS MADE FROM THEM

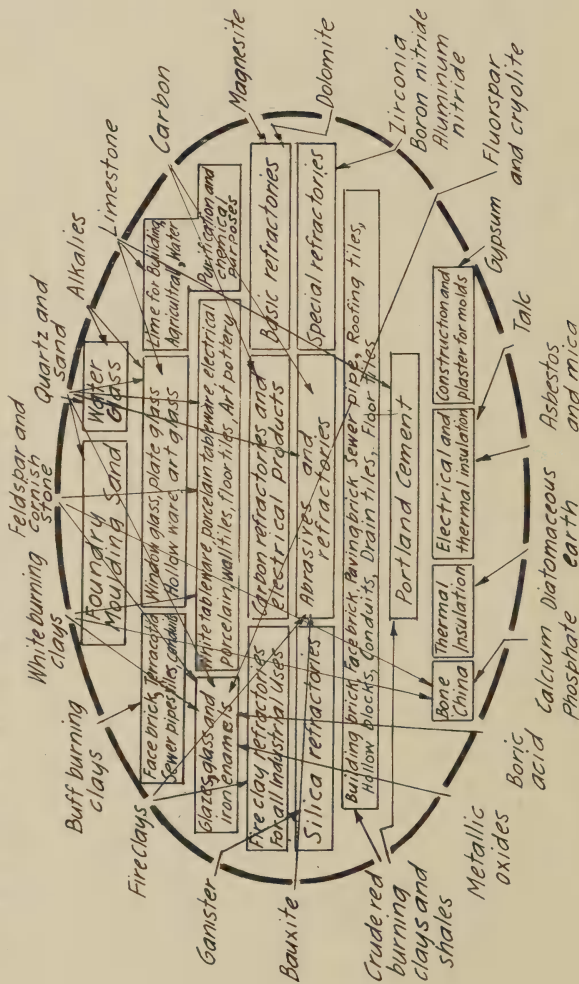


CHART No. 5.

DEPENDENT INDUSTRIES AND THE CERAMIC PRODUCTS UPON WHICH THEY DEPEND

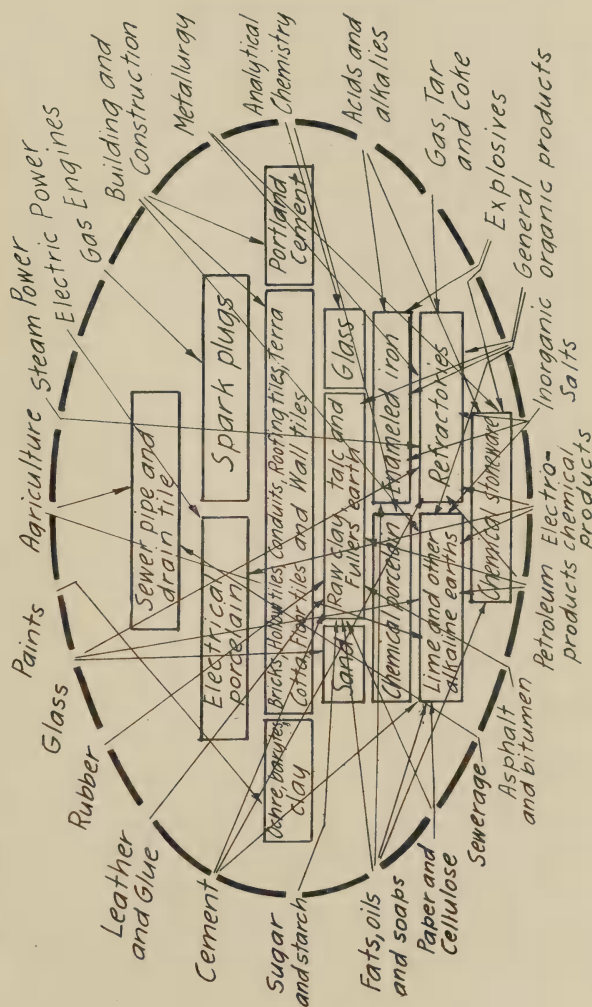


CHART No. 6.

THE CERAMIC INDUSTRIES

A CLASSIFIED LIST OF THE BETTER KNOWN BRANCHES OF THE CERAMIC INDUSTRIES

CLAYWARES

Building brick
Face brick
Paving brick
Terra cotta
Hollow tile
Art pottery
Whitetableware
Porcelain tableware
Bone China
Insulation-heat
Electrical
Cooking ware
Refractories for
Furnace work
all industries
Fire brick
Electrical porcelain
Crucibles
Chemical porcelain
Retorts
Roofing tile
Floor tile
Wall tile
Glass pipes & blocks
Drain tile
Sewer pipe
Conduits
Spark plugs
Sanitary ware
Chemical stoneware

GLASS

Window glass
Plate glass
Hollow ware
Optical glass
Lenses
Chemical glassware
Water glass
Insulation
Art glass
Vault lights
Electric light bulbs
Lighting shades & reflectors

CEMENT

Portland cement
Natural cement
Slag cement

ENAMELLED WARE

Enamelled iron
Enamelled sheet steel
Enamelled insulation,
Enamelled jewelry

ABRASIVES

Emery
Corundum
Sand
Garnet
Artificial abrasives,
Chiefly Al_2O_3 and SiC

SPECIAL REFRACTORIES

Silica brick
Quartzite brick
Magnesia products
Alumina products
Dolomite products
S.C. products
Pyrometer tubes

LIME

Limestone
Crushed rock
Quick lime
Hydrated lime
Agricultural lime
Chemical lime

GYP SUM PRODUCTS

Wall plasters
Moulding plasters
Fertilizer materials
Plaster cements

MISCELLANEOUS

Ochre
Baryles
Talc
Rouge
Pumice
Intusorial
Earth
Sand
Quartz glass

VITAL WAR PRODUCTS

OF THE CERAMIC INDUSTRIES

A FEW OF THE PRODUCTS AND A FEW OF THE USES NEW PRODUCTS

NEW REFRACTORIES *for Destroyers and other Battle Craft*
NEW SPARK PLUGS *for Air-plane engines. Aradical development*
OPTICAL GLASS *for gun lights, Range finders, Binoculars, Periscopes, etc.*
SPECTACLE GLASS *for Spectacle lenses, Reading glasses and Simple magnifiers*
SPECIAL GLASS *for searchlight reflectors, Port lights, etc.*
LABORATORY GLASSWARE AND PORCELAIN *for control work in all industries*

STAPLE PRODUCTS

FIRE BRICK *for Iron and Steel works, Foundries, Glass plants, etc.*
ABRASIVES *for grinding optical products, Munitions, Machine parts, etc.*
CHEMICAL STONEWARE *for making Acids, Heavy chemicals, Explosives, etc.*
PORTLAND CEMENT *for Ships, Building construction, etc.*
LIME STONE AND LIME *for Blast furnaces, Chemical plants and Buildings*
BUILDING BRICKS AND PRODUCTS *for Factory and Government construction work*
ENAMELLED WARE *Iron for Chemical and explosive plants; Steel for Hospital, Camp kitchen, Gallery uses, etc.*

CHART NO. 8.

two relationships are shown in two of the charts (Nos. 5 and 6), which have been reproduced, but it is obvious that it has not been possible to include in such condensed form anything like a complete list, either of the raw materials and their uses, or of the other industries dependent upon ceramic products. There are, however, many very interesting points shown. We are apt to forget that the manufacture of explosives is absolutely dependent upon chemical stoneware and enameled iron with which to carry on the manufacturing processes; that gas engines are useless without spark plugs; that all metallurgical processes, especially our iron and steel industries, are dependent upon serviceable refractories; that our ability to live comfortably in houses depends upon glass for windows; that our entire city life is based on good sanitation which is made possible only by the use of ceramic products in the sewerage systems, etc. This dependency upon the ceramic industries might be shown in almost innumerable instances, but even the limited number shown in the charts is a very convincing argument of the vital need of ceramic products in our modern scheme of life.

The chart (No. 7) listing the better known branches of the ceramic industry is self-explanatory, but the one (No. 8) which tabulates a few of the vital War products calls for a little further discussion. From what has been said in connection with the other charts, it is quite plain that any list that pretends to give, with any degree of completeness, the ceramic products vital to the prosecution of the War, would necessarily be a very long and complicated one, but in order to bring to public attention a few of the most obvious or newest products the chart of Vital War Products was prepared. Ordinarily, one would not think of the refractories in the boiler room of any of our battle-craft as being of more than passing import, but this problem has been exceedingly critical and has now been satisfactorily solved. For airplane engines, a new and better spark plug was required, and it has been and is being produced. Optical glass has had national attention and everyone is familiar with the story of the American manufacturer having successfully produced the required types, qualities and quantities, so that optical glass is not a limiting feature in the National War program. Labora-

tory glassware and porcelain of American make are now available in satisfactory quantity and of good quality. And so the list could be extended to the limit of space available, or to the limit of the reader's patience, but the importance of these vital products should be indelibly impressed upon the public at large so that public opinion will see to it that in future Governmental action these all-important industries are thoroughly appreciated and their encouragement and continuance thereby guaranteed.

ORIGINAL PAPERS AND DISCUSSIONS.

THE POROSITY AND VOLUME CHANGES OF CLAY FIRE BRICK AT FURNACE TEMPERATURES.¹

BY GEORGE A. LOOMIS.

I. Introduction.

General Considerations Regarding the Testing of Fire Bricks.—The testing and classification of clay fire bricks is a subject which has received considerable attention in recent years, but which has not been worked out as yet—to any great degree of completeness. Failure to satisfactorily classify clay fire bricks has been due in part to the fact that clay refractories are used under such a variety of conditions. A fire brick which proves very satisfactory under certain conditions of use may not be able to fulfill the requirements for other uses. Fire bricks may be called upon to resist deformation under excessive or very light loads at high temperatures, to resist sudden changes in temperature, to withstand the intrusion of slags or glasses, to resist abrasive action, and many other equally severe conditions. Obviously, no brick could be expected to withstand all of these conditions perfectly, and it would be hardly fair to condemn a brick, for all purposes, because of its failure to withstand any one of the above conditions. However, it is generally conceded that refractoriness is a primary requisite of a fire brick for general use and the other properties, such as ability to resist abrasion or the penetration of slags, may be said to be of secondary importance. Therefore, the question of the satisfactory evaluation of refractoriness has proven the main problem in the testing and classification of clay fire bricks.

¹ By permission of the Director, Bureau of Standards.

The Measurement of Refractoriness.—In working out a satisfactory classification of fire bricks based on refractoriness, several tests for the measurement of this property have been put into more or less general use. Of these, the three which have been used the most are, first, the chemical analysis, which gives a theoretical indication of refractoriness, second, the direct determination of the so-called "softening point," and third, the determination by an actual "load test" of the ability of a fire brick to resist deformation under loads at high temperatures. These tests will be described more in detail later. Another test, as a measurement of refractoriness, but which has not been used very extensively in the case of fire bricks, is the determination of the porosity and volume changes on heating the bricks to different temperatures. A decrease in porosity and volume indicates the progress toward vitrification, and when these changes are plotted in the form of curves, the slope of the curves shows the rate of vitrification. Over-firing is then indicated by an increase in porosity and by an increase in volume as the vesicular structure accompanying over-firing is developed. A classification of fire clays, based on porosity changes, was first suggested by Purdy,¹ who set the limits for the different grades of refractories. These limits have since been found to be in error but nevertheless the idea of measuring the refractoriness of a fire brick by its changes in porosity and volume is evidently a sound one.

Temperature-Porosity Changes as an Indication of Load Carrying Ability.—The value of the porosity and volume change determinations is all the more evident when it is realized that the degree of vitrification, as shown by the changes in porosity, also represents the amount of softening which must necessarily take place in the process of vitrification. Marked softening of the mass of the brick means decreased resistance to deformation. In other words, the changes in porosity may be said to bear some relation to the resistance to deformation of a brick under load at high temperatures.

Object of Present Investigation.—From the above considerations it is evident that the determination of the porosity

¹ *U. S. Geol. Surv. Bull.*, 9, p. 111.

and volume changes is very valuable in the study of the fundamental properties of clay fire bricks and it is only by a better knowledge of the fundamental properties that a completely satisfactory classification of fire bricks can be worked out. The present investigation was, therefore, undertaken in order to study the fundamental properties of clay fire bricks by a comparison of their changes in porosity and volume, upon heating to different temperatures, with the results of a specific load test and with the so-called "softening points." Preliminary work on this investigation was first undertaken under the direction of G. H. Brown, when connected with the Bureau of Standards. It was afterward decided to take up the investigation on a larger scale, with the coöperation of the Refractories Manufacturers' Association, which kindly furnished samples of a great number of brands of fire brick for the tests, and likewise in the interest of the American Gas Institute.

II. Description of Fire Brick Tests Already Used.

Before taking up the details of the present investigation, it is well to describe and discuss briefly the most noteworthy tests which are being used in determining the value of clay fire bricks—including the tests which have already been mentioned.

Chemical Analysis.—The chemical analysis has been used to quite an extent in the study of the fundamental properties of fire bricks and is of considerable value—not only in this regard but also in explaining the causes of failure in use. The chemical analysis serves as an indication of the refractoriness by showing the degree of purity of the clay. Clay of the purest type possible, *i. e.*, pure kaolin, has a softening temperature or so-called "melting point," of $1740^{\circ}\text{C}.$ ¹ This purest form of clay has a composition corresponding to that of the mineral kaolinite, being composed of 46.3 per cent silica, 39.8 per cent alumina and 13.9 per cent chemically combined water. In burning, this chemical water is driven off and the composition becomes 53.8 per cent silica and 46.2 per cent alumina. Clay of this composition is of comparatively rare occurrence, owing to the presence, in most

¹ *Bur. Standards, Tech. Paper, 10.*

cases, of quartz, feldspar, magnesia, lime and iron oxide, in varying amounts, and which behave as fluxes in lowering the softening point of the clay to a greater or less extent. Some attempts have been made to apply the chemical analysis directly as a measure of refractoriness, by means of formulas, but these have not been in any degree satisfactory. The determination of the amount of these fluxes by a chemical analysis may, however, be considered as an aid in determining the refractoriness of the clay, as well as serving in some measure to explain the failures of fire clay brick in use.

A classification of fire bricks based on the chemical analysis has been proposed¹—which fixes the limit for the permissible amount of fluxes for No. 1 grade bricks. According to this classification, the total amount of fluxes must not exceed 0.22 molecular equivalents. This expression for the amount of fluxes is a part of the empirical formula commonly used in the study of ceramic bodies. This is calculated from the chemical analysis, by dividing the respective percentages by the molecular weights of the oxides, then dividing each value obtained by the value for the alumina. The values for the various fluxes are then summed up and the formula obtained is of the type $x\text{SiO}_2 \cdot y\text{Al}_2\text{O}_3 \cdot z\text{RO}$. In this formula, determined for fire bricks, the RO equivalent must not exceed 0.22 for the No. 1 fire bricks, according to the suggested classification. In the case of the silicious clay brick (say one containing 65 per cent or more of silica) the permissible amount of fluxes is considerably less—since the fluxes are more effective upon silicious material. It is quite evident, then, that the chemical analysis is of some value in studying the causes of failure of refractories. However, there are physical tests which require less time to perform than the chemical analysis and yet which indicate much more satisfactorily the value of a fire brick in a practical manner.

Softening Point.—The determination of the so-called “softening point” is one of the most widely used tests for fire bricks and is generally considered a reliable indication of the refractoriness of the material. In determining the softening point, small tetra-

¹ *Bur. Standards Tech. Paper, 7.*

hedra, of the size of the well-known Orton standard higher pyrometric cones, are molded from a portion of the brick, ground to pass about an eighty-mesh screen, and mixed with a gum of tragacanth solution to serve as a temporary bond. These are then set in a suitable plaque of refractory clay material beside a series of standard pyrometric cones and heated in a carbon resistance electric furnace, or a small pot furnace heated with a gas-blast burner of the Fletcher type. The "softening point" is indicated by the point at which the test cone deforms to the extent that the tip is on a level with the base or the cone has swelled excessively. Results are expressed in terms of the standard cone which has deformed to the same extent. Temperatures are not usually considered—since it is a well-known fact that the bending of the standard cones is affected by the rate of heating. However, very good comparative results are obtained by limiting the time of firing in such a test to an hour and a half or two hours.

In classifying fire bricks according to the softening point, cone 30 is usually considered the lowest value for No. 1 grade, cone 30 to 28 for No. 2 grade, and cone 28 to 26 for No. 3 grade. This classification is, no doubt, a proper one but at the same time it quite often proves misleading, in so far that the bricks with a higher softening point, cone 32 or above, sometimes fail to withstand practical conditions of load and temperature while silicious bricks, low in fluxes, with a softening point as low as cone 29, generally stand up well under heavy loads at fairly high temperatures. This is explained by the fact that silicious bricks remain quite rigid to within about 100°C of their softening points while the brick lower in silica soften through a longer range. Then, too, the softening point determination is misleading in the case of bricks made from a coarse mixture of very refractory non-plastic clay (flint clay) with an inferior bond clay. The comparatively fine grinding necessary to molding the cone brings about a more intimate mixture of the material so that the refractoriness is raised. This objectionable feature of the softening point test is sometimes overcome by using a chip of the original brick—cut on a carborundum wheel to the form and size of the standard cones. This, however, is often a difficult task and is practically impossible in the case of a very coarse friable material,

to say nothing of the variation in the results arising from not obtaining an average sample from so small a specimen.

The Load Test.—What is known as the standardized "load test" was first used by the Bureau of Standards in an investigation of clay refractories. This test has proven the most practical and surest means of determining the behavior of fire bricks in use under high loads and temperatures. The test is generally performed upon a brick of standard size and shape, placed on end in a specially designed furnace of about $20'' \times 20'' \times 20''$ internal dimensions. The load is applied to the brick longitudinally, through a suitable opening in the top of the kiln, by means of a highly refractory column on which rests a horizontal beam. On the furnace used by the Bureau of Standards, this beam rests upon a knife edge on the column and acts as a lever fastened and adjustable at one end to keep it level, and the load is applied at the other end. On a later type of load test furnace, the beam is balanced by applying an equal load on both ends and no knife edge is used. The firing, in the case of the Bureau of Standards furnace, is done by means of eight Fletcher gas-blast burners, two on each side, and four in front. In conducting this test, the temperature is raised at a specified rate to the maximum temperature, which is held for one hour and a half. It has been found that 1350°C is the most suitable maximum temperature in testing first grade fire bricks. A load of 40 pounds per square inch has been used, although this is rather severe and one of 25 pounds per square inch is believed a fairer test for No. 1 brick.

Although there are no standard specifications for clay fire bricks as yet, one-half inch contraction in a length of nine-inch brick is considered the permissible limit for a No. 1 refractory after testing under a load of 40 pounds per square inch at 1350°C . All fire clay bricks, which have not deformed more than one-half inch in such a test, have proven very satisfactory in use under average loads at temperatures not exceeding 1350°C . Hence, there seems to be no doubt whatever of the practical value of the load test. It may be a little too severe in rejecting bricks which might prove satisfactory in use, but this fault is easily remedied by decreasing the load applied. However, there is

one objection to the load test. This is the matter of time required for its performance—since only one brick can be tested in the furnace at a time and each test requires about six hours time to perform. This is quite a serious objection when only one test kiln is available and the results on a large number of bricks are needed in a short time.

Cold Crushing Test.—This test is a rather valuable one in eliminating unsatisfactory bricks from consideration for use under loads at high temperatures. Obviously, a refractory possesses but a small part of its cold crushing strength when at a temperature of 1350°C , and if a brick has a low crushing strength when cold, it is almost certain to fail in a load test at 1350°C . It has been found that a cold crushing strength of 1000 pounds per square inch, when the brick is tested on end, is about the lowest permissible value in this regard. Needless to say, a high capacity compressive strength testing machine is necessary in performing this test.

The Ball Test.—A special form of load test, called the "ball test," has been put into use by Unger and Nesbitt, of the Carnegie Steel Company.¹ This test was devised in attempting to find a substitute for the regular load test and which could be performed on a larger number of bricks in a short time. It is claimed that the results compare favorably with those of the regular load test. The test is made by heating bricks to 1350°C for one hour in a furnace, drawing them out quickly and laying them on their side under a long lever in such a manner that a two-inch iron ball, placed on the brick under the lever, is depressed into the face as increasing pressure is applied to the lever. A certain load is applied which is gradually brought up to a maximum in about five minutes. The depression made by the ball is measured in inches. The proper load to give a depression comparable to the contraction in a regular load test was determined by experiment. There is no doubt that such a test can be made on a number of bricks in much less time than is required by the regular load test. However, there is some objection to it as a regular test for fire bricks on the ground that cooling takes place sufficiently during

¹ *Proc. Eng. Soc. Western Penn.*, 32, No. 7.

the test to influence the results. Then, too, the portion of the brick receiving the pressure is a small part of the whole brick and the results are apt to be affected by small local defects in the structure of the brick.

The special tests of fire bricks, such as the determination of the resistance to slagging action, the resistance to impact and abrasion, and the test of ability to withstand sudden temperature changes, have little or no connection with the present investigation and need not be described here.^{1,2}

III. Method of Study of Porosity and Volume Changes in Connection with Load Tests and Softening Points.

Determination of Porosity and Volume Changes.—Taking up the details of the present investigation, the porosity and volume changes of the fire bricks, for comparison with the results of load tests and softening points, were determined in the following manner: Specimens of each brand of fire brick were cut with a broad chisel into briquettes, approximately $2\frac{1}{2} \times 1\frac{1}{4} \times 1\frac{1}{4}$ inches in size, squared up somewhat on a grinding wheel, and suitably marked with a cobalt paint—made by mixing powdered cobalt oxide, one part, and kaolin, three parts, in water. Six briquettes were cut for each brand. A neater method of cutting the specimens would have been to use a carborundum cutting wheel. However, the method used was quicker and equally as good except for the appearance of the specimens.

The initial porosity was then determined on two of these small specimens from each brand—by first weighing the specimens to 0.10 g. after drying at 110°C , then determining the wet weight and the suspended weight after soaking in boiling water under a vacuum, represented by a 24-inch mercury column, for four hours. The per cent porosity was then determined from the usual formula

$$\frac{\text{Wet weight} - \text{dry weight}}{\text{Wet weight} - \text{suspended weight}} \times 100 = \text{per cent porosity.}$$

¹ For description of these special tests see Nesbitt and Bell, "Practical Methods for Testing Refractory Fire Bricks," *Proc. Am. Soc. Testing Materials*, **16**, 349, Part 2.

² Brown, "Methods of Testing Corrosive Action of Slags," *Trans. Am. Ceram. Soc.*, **18**, 277, (1916).

The volumes of the six briquettes of each brand were then accurately determined in a voluminometer of the Seger type, after soaking the specimens in oil. Duplicate determinations of each volume were made to obtain a check within 0.2 cc.

The six briquettes of each brand were then set for re-burning in a muffle in a test kiln in such a manner that a specimen for each brand could be drawn at regular intervals in the process of firing. Space was left between each set of draws and between the individual piles to allow the equal heating of all briquettes. A set of pyrometric cones and a thermocouple in a porcelain protecting tube were placed inside the muffle beside the briquettes. With this arrangement, the size of the muffle permitted the burning of 84 specimens from 14 brands at one time.

In burning the briquettes, the temperature was brought rapidly up to 250° – 300° C and held for three or four hours—in order to vaporize the oil in the briquettes (without igniting and leaving carbon to influence the results by the reduction of the iron). Over night, the temperature was brought up to 800° C, this being the highest temperature that could be attained in this kiln without the use of compressed air—which was not usually available at night. From 800° C the temperature was raised rapidly to 1200° C. The temperature was then increased at the rate of 30° C per hour from 1200° to 1500° C. The draws were made at 50° intervals between 1250° and 1500° C, and were cooled slowly by covering with hot sand in a suitable container.

The deformation of the standard cones, as observed during the firing of the briquettes, was as follows:

Cone 13 down at 1350° C	
Cone 15 down at 1450° C	
Cone 17 down at	} 1500° C
Cone 18 half down at	

As usual, a cone was considered down when the tip was on a level with the base. It may be well to note here that cones, when used in a burn of this kind, are retarded slightly, owing to the cooling unavoidably given them in making the draws.

After the burning of the briquettes, the porosity of each was determined by the same method used in determining the initial porosities. It may be said in regard to the method of soaking

the specimens, that placing them in boiling water under vacuum for four hours gave more consistent results than the usual method of simply boiling in water. It was found that results could be checked exactly on the same specimen by the vacuum method, whereas, results by the boiling test alone were found to be sometimes as much as three points lower than by the vacuum method.

The final volumes of the briquettes were determined in the voluminometer in the same manner as the initial volumes—duplicate determinations on the same briquettes being checked to 0.2 cc. The volume change was computed in terms of the initial volume. The volume changes and porosities at the different temperatures were plotted in the form of curves for each brand of brick.

Method of Making Load Test.—The regular load test was made on a full-size specimen of each brand (standard size bricks used) employing a load of 40 pounds per square inch at a temperature of 1350°C for an hour and a half. The load of 40 pounds per square inch was considered best for testing first grade fire bricks at the time the tests were made, although one of 25 pounds per square inch is now generally considered as best.

The kiln used for the load test was the one which has already been described. Special care was used during these tests to keep the beam level at all times in order to prevent eccentric loading on the specimen. The usual rate of firing up to 1350°C was followed. It is given in Table I.

TABLE I.—SCHEDULE OF FIRING IN LOAD TEST.

Time.		Temperature. Degrees C.	Time.		Temperature. Degrees C.
Hours.	Minutes.		Hours.	Minutes.	
..	15	200	2	45	1160
..	30	370	3	..	1200
..	45	520	3	15	1240
1	..	670	3	30	1270
1	15	800	3	45	1300
1	30	880	4	..	1320
1	45	960	4	15	1340
2	..	1020	4	30	1350
2	15	1070	<hr/> 1350° C held for one hour and a half.		
2	30	1120			

The thermocouple, in a porcelain protecting tube, used in measuring the temperature, was placed within one-half inch of the brick. Cones were also placed close to the brick as a check on the firing—although the couples and instruments used in this test and for the porosity determinations were calibrated against standards, from time to time, to insure accuracy in measuring the temperatures.

When the investigation was first started, the plan was to make duplicate determinations by the load test and to take the average results for comparison with the results of the porosity and volume change determinations. However, the variation in initial porosity on different specimens of the same brand of brick is sometimes quite considerable, due, in most cases, to a difference in burning in manufacture. It was therefore decided to determine the initial porosity on several of the full-size bricks of each brand, in the same manner as was done with the briquettes, and to use the brick for the load test which was found to have the nearest porosity corresponding to that of the briquettes used in the other test. By so doing, it seemed that a good comparison of the results of the load test with those of the porosity and volume change determinations could be made without making duplicate determinations by the load test on each brand. Under the circumstances, it did not seem worth while to take the time for more than one load test on each brand—considering the large number of brands tested.

Method of Determining Softening Points.—The softening-point determinations were made by grinding up portions of the brick to pass a 60-mesh screen and molding with gum of tragacanth into cones as nearly as possible the exact size of the Orton higher pyrometric cones. These were set in a plaque of suitable refractory clay material with a series of pyrometric cones—in the usual manner of determining softening points—and fired in a small pot furnace, using a Fletcher blast burner with natural gas and compressed air. The time of firing in each test was limited to an hour and a half to two hours. The softening point was determined by the point at which the cones bent in the prescribed manner and the result was expressed in terms of the corre-

sponding standard cone. Duplicate determinations of the softening point were made on two bricks of each brand. Practically all of the results agreed within one-fourth of a cone and in no case did duplicate determinations on two bricks differ more than one-half cone.

IV. Discussion of Results.

A study of the data obtained shows some interesting relationships between the porosity and volume changes and the results of the load tests. In nearly all cases of brick which successfully withstood the load test—showing a deformation of not more than 5.55 per cent—there is comparatively little volume change by either expansion or contraction up to 1425°C , while a considerable number of the brick which failed in the load test show very appreciable volume changes. Similarly, the porosity decrease in the case of brick which pass the load test is not large while many of those which failed show considerable decrease in porosity at some point below 1425°C . In many cases, over-burning of the brick of poorer grade is distinctly evident from the volume and porosity changes. The sudden and more or less pronounced expansion at the lower temperatures of firing, in the case of some of the bricks, is certain evidence of over-burning which was confirmed by the results in the load tests. An abrupt increase in porosity at the same or at a slightly higher temperature is usually noted in such cases. Invariably, such brick failed in the load test. Bricks which show either marked volume change or a considerable decrease in porosity also failed to withstand the load test.

It would seem, then, that the volume and porosity changes of clay fire brick might serve in some measure as a criterion of their ability to withstand load at high temperatures. A careful study of the following data for various burning temperatures shows some interesting points in this connection:

1350°C : Of 26 brick which passed in the load test, 23 show not more than 1 per cent volume change, 3 show more than 1 per cent. Of 35 brick failing in the load test (showing more than 5.55 per cent deformation), 16 show not more than 1 per cent volume change and 19 more than 1 per cent.

Of 26 brick passing the load test, 25 show not more than 3 per cent porosity decrease, 1 more than 3 per cent. Of 35 failing in the load tests, 13 show not over 3 per cent and 22 more than 3 per cent porosity decrease.

Combining these criteria, 33 of 61 brick show not more than 1 per cent volume change nor more than 3 per cent porosity decrease—23 of these passing and 10 failing the load test. Of those showing more than 1 per cent volume change or more than 3 per cent decrease in porosity, 3 passed and 25 failed the load tests.

1400° C: Not over 2 per cent volume change was shown by 23 brick which passed and 15 which failed in the load test. Of 23 brick which showed over 2 per cent volume change, 3 passed and 20 failed in the load tests.

Of 36 brick showing not over 5 per cent decrease in porosity, 22 passed and 14 failed in the load test. Of 25 showing more than 5 per cent porosity decrease, 3 passed and 22 failed in the load test.

Of the brick which showed neither a volume change greater than 2 per cent nor a porosity decrease exceeding 5 per cent, 22 passed and 10 failed in the load test.

On the basis of a volume change not exceeding 3 per cent at 1400° C (amounting to about 1 per cent linear expansion or contraction), 24 passed and 19 failed in the load test. Of those exceeding 3 per cent volume change, 2 passed and 16 failed the load tests.

Excluding brick which showed more than 3 per cent volume change or 5 per cent porosity decrease, 22 passed and 10 failed in the load test. Of those which showed either more than 3 per cent volume change or 5 per cent porosity decrease, 4 passed and 25 failed in the load test.

1425° C: Of 38 brick showing not more than 2 per cent volume change, 23 passed and 15 failed the load test. Of those showing more than 2 per cent volume change, 3 passed and 20 failed the load tests.

Of 34 brick showing not over 5 per cent porosity change, 21 passed and 13 failed the load test. Of those showing more than

5 per cent porosity decrease, 6 passed and 21 failed in the load tests.

Of the brick which neither changed more than 2 per cent in volume nor 5 per cent in porosity, 20 passed and 7 failed in the load test. Of those changing more than 2 per cent in volume or 5 per cent in porosity, 6 passed and 28 failed in the load test.

It is apparent that the porosity and volume changes of clay fire brick, when burned at some temperature between 1350° and 1425° C, offers, in some degree, a criterion of their ability to withstand the load test. The bricks passed or rejected by the suggested limitations in porosity or volume changes at the various temperatures are nearly the same in all cases. This consistency indicates that the apparent relation between these changes and the ability of bricks to withstand the load test is more than a chance one and that certain limitations in this respect might well be used as a means of rejection of a large number of bricks which would undoubtedly fail in that test. The use of either porosity or volume changes alone offers a fairly satisfactory criterion. Taken together, the result is even better—since a number of brick failing in the load test can pass one or the other specification as regards volume or porosity changes but few of the better bricks fail to pass both.

For practical purposes, a temperature should be selected which is not too high to be readily attained under ordinary conditions, but high enough that the limitations in porosity or volume changes need not be too close to be easily measured. The use of linear measurements of expansion or contraction rather than volume measurements, would be extremely desirable from the standpoint of simplicity. From the results here obtained, a temperature of 1400° C would seem most satisfactory since the permissible limit in volume change may be made as high as 3 per cent—this practically amounting to a linear contraction or expansion of 1 per cent. A limit of 5 per cent in porosity decrease is also quite satisfactory. At this temperature also the effects of over-burning in the inferior materials is likely to become sufficiently evident to be readily detected. Nearly all of the bricks which successfully withstand the load test could meet these specifications while a majority of those that fail under load would be elim-

inated by excessive volume or porosity change, or both. It may be noted that in all cases brick which showed a porosity decrease exceeding 5 per cent, or a volume change exceeding 3 per cent, showed a deformation in excess of 5 per cent in the load test—close to the permissible limit.

In the case of clay fire brick, an increase in volume is especially significant, as it represents evidence showing that over-firing has taken place—due to a comparatively high content of fluxes. It is important, therefore, that the permissible expansion be rigidly limited to a definite value which must be lower than that for the allowable contraction.

In the case of some of the brick failing in the load test—due to failure of the bond—there were no marked changes in either volume or porosity. Generally, such brick have a very low, cold crushing strength—as in the case of one brick which failed under a load of 364 lbs. per square inch and another which crushed at 385 lbs. per square inch. The minimum allowable cold crushing strength for a No. 1 refractory is generally placed at 1000 lbs. per sq. inch.

There is apparently little relation between the softening points and the volume and porosity changes or with the results of the load test. Some of the brick, showing high softening temperatures, failed to withstand this test while several which softened below cone 31 showed less than 5 per cent deformation. The latter were probably silicious in character, containing more than 65 per cent SiO_2 . In some cases where brick failed, the high softening point is probably due to the intimate mixture of the inferior bonding clay with the more refractory flint clay in the preparation of the test cones—the material being ground to 60-mesh size. In all cases, brick showing softening points lower than cone 28 failed completely in the load test. It may be considered then that cone 28 should be the minimum softening temperature of a No. 1 refractory of either silicious or non-silicious character.

In Fig. 1 are shown porosity and volume change curves for six bricks of different characteristics which successfully withstood the load test. These have been selected as fairly typical of the

bricks of this class. Contraction is indicated by negative volume change, expansion by positive values.

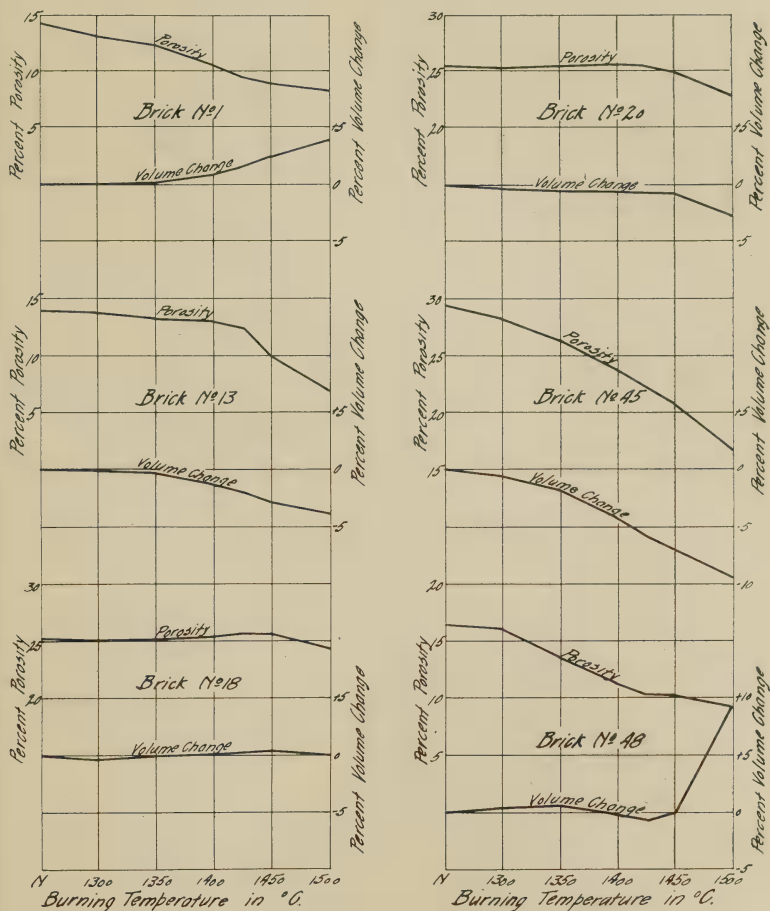


FIG. 1.

In the curves for brick No. 1 a gradual expansion, accompanied by a gradual decrease in porosity, is noted. The low initial porosity is characteristic of the stiff-mud brick. The gradual expansion would seem to indicate a silicious character, but this

seems unlikely in view of the high softening point, cone 32. The result of the load test was a deformation of 4.47 per cent.

Brick No. 13 shows gradual contraction beyond 1350°C —accompanied by an increased rate of porosity decrease above 1425°C . This is also a stiff-mud brick with low initial porosity and a softening point of cone $31^{3}/_{4}$. The deformation in the load test was slight, only 1.06 per cent.

Brick No. 18, made by dry pressing, is apparently silicious in character—as indicated by the slight expansion on heating and the very slight porosity changes. The slight deformation in the load test, 0.11 per cent, and the softening temperature of cone $29^{1}/_{4}$, which is too low for a non-silicious material of this quality, also indicate a high silica content. The chemical analysis shows 80.56 per cent SiO_2 and a very low content of fluxes.

Brick No. 20, hand made from a mixture of flint and plastic clays, represents a high clay brick of excellent refractoriness. The porosity curve shows the characteristics of flint clays—in the slight changes up to 1425°C . No appreciable volume change occurs below 1450°C . The softening point was cone 32 and the deformation in the load test was only 1.62 per cent.

Brick No. 45 showed a deformation of 5.33 per cent in the load test—close to the allowable limit. The large amounts of contraction and porosity decrease would render the quality of this brick doubtful in the light of the suggested specifications in this respect. The regularity of the porosity decrease and contraction indicates a gradual and continuous fluxing action but with no indication of over-burning. The softening point of this material was cone 31.

Brick No. 48 shows a rapid porosity decrease above 1300°C . The volume change is slight up to 1425°C , where over-burning is indicated by the subsequent expansion. While the deformation in the load test (4.47 per cent) fell within the limit, the porosity change exceeds 5 per cent. The ability of this brick to withstand a long-continued heat treatment at high temperatures would be somewhat doubtful—due to its over-burning tendencies. The softening point was at cone $31^{1}/_{4}$.

In Fig. 2 are shown curves for some of the brick which failed to pass the load tests. Brick No. 26, with a deformation of 12.6

per cent, shows a gradual expansion above 1300°C , becoming rapid above 1400°C . The increase in porosity at 1425°C indicates that this is probably due to the gradual development of a vesicular structure by over-burning.

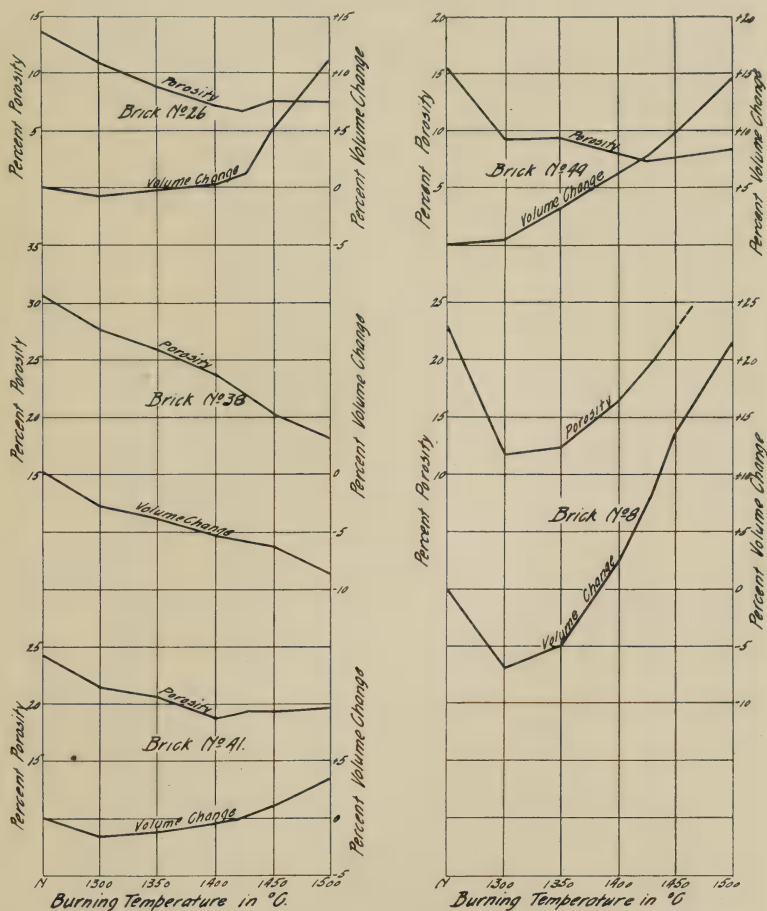


FIG. 2.

Brick No. 38 shows marked but gradual fluxing in its rapid decrease in both porosity and volume. It is evidently not of silicious character and of only fair refractoriness. The softening

point at cone $30\frac{1}{4}$ and the deformation in the load test (10.4 per cent) confirms this.

Brick No. 41 begins to over-burn at 1300°C , as indicated by the expansion and by the break in the porosity curve at a somewhat higher temperature. The high softening point, cone $33\frac{1}{2}$, is apparently the result of the fine grinding of the material in preparing the test cones. The failure to pass the load test was probably due to an inferior bond clay in the mixture.

Brick No. 49, also made from a mixture of clays, shows over-burning by the expansion above 1300°C and the break in the porosity curve. The softening point is at cone $31\frac{1}{4}$ and the deformation in the load test was 9.37 per cent.

Brick No. 8 is typical of a number of those which failed completely in the load test. It has a low softening point (cone $27\frac{1}{2}$) and shows marked over-burning above 1300°C , as indicated by the rapid expansion and by the increase in porosity. The decided contraction and decrease in porosity when burned at 1300°C indicate a low temperature of burning in manufacture.

V. Suggestions for the Practical Application of Porosity and Volume Changes of Clay Fire Brick.

The determination of the porosity or volume changes of clay fire brick, burned at some temperature between 1350°C and 1425°C , affords a means of classifying a certain proportion of brick which would fail in the load test. The limit of 3 per cent in volume change (or 1 per cent in linear contraction or expansion) and 5 per cent decrease in porosity at 1400°C , does not eliminate all brick which cannot withstand such a test, but materially reduces the number which would require such testing. In this respect, it would be of considerable advantage in comparing the quality of a large number of samples—since the porosity and volume changes may be determined readily from a single burn in a test kiln. To make standard load tests on a number of brick requires considerable time and expense even if several furnaces are available.

The determination of volume changes is comparatively simple when porosities are also determined—since the difference in the wet and suspended weights of the specimens affords a measure-

ment of volume practically as accurate as determinations by means of the voluminometer.

The porosity and volume changes in burning may also be used advantageously as a means of determining the uniformity of quality of a lot of bricks of a single brand. The behavior of such bricks should be fairly uniform if they are of equal quality. Such applications of these measurements would be of value to the manufacturer as well as to the consumer.

A study of the curves for porosity and volume changes for a series of burning temperatures offers a means of determining, in some measure, the causes of failure of certain brick in the load test. If this is due to under-burning, resulting in excessive deformation under load—due to shrinkage—a considerable decrease in porosity and volume will be found at the lower burning temperatures. Clays of inferior quality, which over-burn, will be detected by a marked expansion at some point in the burning, usually accompanied at a somewhat higher temperature by an increase in porosity—due to the development of a vesicular structure. Clays high in fluxes, but which do not readily develop a vesicular structure, show gradual but marked contraction and decrease in porosity as the burning temperature is increased.

VI. Summary.

1. Brick which are capable of withstanding a pressure of 40 lbs. per square inch at 1350°C generally show slight changes in volume or in porosity when burned at temperatures up to 1425°C .
2. The greater number of the brick which failed to pass the load tests show rather marked changes in volume or in porosity at some temperature below 1425°C .
3. Brick which show distinct over-burning by pronounced expansion at temperatures below 1400°C invariably fail in the load test. The adoption of a definite limit for the permissible expansion within the given temperature range is particularly important for detecting inferior clay refractories. The limit for expansion should be lower than that for allowable contraction.
4. The changes in volume and in porosity of brick burned at some temperature between 1350°C and 1425°C serves, in a measure, as a criterion of their ability to pass the load test.

5. Most of the brick which show a porosity decrease not exceeding 5 per cent and a volume change not exceeding 3 per cent (approximately 1 per cent in linear dimensions), when burned at 1400°C will pass the load test.

6. Brick which show a decrease in porosity exceeding 5 per cent or an expansion or contraction in excess of 3 per cent by volume (1 per cent in length) at 1400°C failed to pass the load test in nearly all cases.

7. The use of limiting porosity and volume changes for clay fire brick burned at 1400°C would serve as a means of eliminating from consideration a large number of brick which fail in the load tests.

8. Brick which fail in the load test—due to failure in the bond—may not show marked changes in volume or porosity in burning but often show very low cold crushing strength.

9. No definite relationship seems to exist between the softening point of a fire brick and its ability to withstand load at high temperatures. However, all brick which softened below cone 28, whether silicious in character or not, failed completely in the load test. It seems advisable, then, to specify cone 28 as the minimum softening point for any clay fire brick. It is probable that brick containing less than 65 per cent SiO_2 should have a minimum softening point of cone 31.

In conclusion, the writer desires to express his appreciation of the assistance rendered by Mr. D. W. Ross in conducting the load tests of this investigation and to thank Mr. A. V. Bleininger for valuable suggestions in carrying out the work.

THE CALCULATION OF THE "RATIONAL ANALYSIS" OF CLAYS.

BY HENRY S. WASHINGTON.

Introduction.

There are comparatively few clays used in the ceramic industries which consist of pure kaolin, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, or of those other closely similar hydrated aluminum silicates, which, collectively, have been called "clay substance" and by other similar names.¹ By far the greater number of clays contain other minerals as well; of these, the most important are quartz, feldspars, and micas. The two most common micas, the purely potassic muscovite and the ferro-magnesian biotite, are, however, not present in large amount in any but a few clays that are of commercial value, particularly for the finer ceramic purposes. Besides the above-named minerals, numerous other minerals have been observed in clays,² but these, almost without exception, are present in such small amounts in clays of any notable commercial value that they may be regarded as practically negligible.

Only four minerals, then, kaolin, quartz, feldspar, and mica, need be considered for the present. As each of these influences the "burning" and other properties of a clay and of the finished products, it is of importance to be able to estimate the relative amounts of each present in any given clay, so that the proper mixtures may be made or the proper temperature and other conditions may be controlled. The ceramist endeavors to accomplish this by what is known technically as the "rational" analysis.³

¹ K. Langenbeck, "The Chemistry of Pottery," Easton, 1895, p. 11; J. W. Mellor, "A Treatise on Quantitative Inorganic Analysis," London, 1913, p. 656; H. Ries, "Clays, Their Occurrence, Properties and Uses," New York, 1914, p. 5.

² Mellor, "Quant. Anal.," p. 656; Ries, "Clays," pp. 56ff.

³ As will be seen, I am quite in agreement with Mellor ("Clay and Pottery Industries," 1914, I, p. 109, in his low opinion of the "rational" analysis and in his view that the adjective is misapplied.

The "rational" analysis aims at the estimation of the amounts of the different minerals that are present in a clay; the object of the "ultimate" analysis is to determine the amounts of the chemical constituents of the clay, quite irrespective of the mineral forms in which they may occur.

The "rational" analysis seeks to attain its object by treatment of the clay with various strong reagents, particularly hydrochloric and sulphuric acids and alkali hydroxides. The methods and details of manipulation differ somewhat,¹ and the results of the ultimate analyses are frequently used in conjunction with the data so obtained.

Following Mellor, the essential features of the "rational" analysis are: digestion of the clay with hot, concentrated sulphuric acid and subsequent washing alternately with alkali and hydrochloric acid, to remove the "clay substance;" this may be preceded by treatment with hot alkali to remove soluble silica, or with dilute hydrochloric acid, to remove the carbonates; and it may be followed by evaporation of the residue with hydrofluoric acid to remove quartz and other silica, and determination of the alumina, which is used as a basis for the calculation of the feldspar present.

There is great divergence of opinion, even among ceramists themselves,² as to the value of the "rational" analysis, a crude form of which was in use as early as the end of the eighteenth century.³ It is unnecessary, within the scope of this paper, to discuss the details of the various modifications which "rational" analysis has assumed, and it must suffice to point out a few general truths that are applicable to the methods in all forms of "rational" analysis, and that are self-evident to the mineralogist or to the chemist who has had experience in the quantitative chemical analysis of silicates.

¹ For descriptions of the methods of "rational" analysis of clays see H. A. Seger, "Collected Works," Easton, Penna., 1902, I, p. 50; Binns, Zimmer and Orton, *Trans. Am. Ceram. Soc.*, **2**, 221 (1900); H. Bollenbach, *Sprechsaal*, 1908, No. 25, p. 340; No. 26, p. 351; Mellor, "Quant. Anal.," 1913, p. 658; Ries, "Clays," 1914, p. 75; A. S. Watts, *Bur. Mines Bull.*, **53**, 38 (1913).

² For some discussions of the value of "rational" analyses, see C. F. Binns, *Trans. Am. Ceram. Soc.*, **8**, 198 (1906); R. C. Purdy, *Ibid.*, **14**, 359 (1912); J. W. Mellor, "Clay and Pottery Industries," 1914, p. 109.

³ Mellor, "Quant. Anal.," p. 657.

Some, though comparatively few, researches have been made into the action of the various reagents used in "rational" analysis on the different minerals present in clays, particularly kaolin,¹ quartz, feldspar, and mica. These researches have neglected to take into account all of the factors that may have a great controlling influence on the ultimate effect of the reagents.

Foremost among these factors is the chemical composition of the mineral treated. The "feldspar" in a clay may be the potassic orthoclase, which is, other conditions being alike, only slightly attacked by strong acids. It may be one of the series of the plagioclases, or soda-lime feldspars, which in solubility relations vary continuously from the purely sodic albite, which is about as insoluble as orthoclase, through the sodi-calcic labradorite, which is somewhat soluble, to the purely calcic anorthite, which is readily soluble, even in rather weak acid. The different micas, also, vary in solubility, muscovite being attacked with some difficulty, while biotite is much more readily dissolved, the different varieties of this also varying in their behavior. Kaolin itself varies in its resistance to reagents, both acid and alkali,² with its origin, the kind and concentration of acid, and other conditions. The different varieties of silica which may be present in clays vary in their resistance to different reagents.

Another important factor is the size of grain, which influences very much the extent and the rapidity of attack or solution of a mineral by reagents or solvents. It is well known that the smaller the particles of a substance the more rapidly it dissolves, the relation depending on the truth that the area of a sphere diminishes as the square, and the volume or mass as the cube, of the radius. The difference in rate of solution with size of grain is accentuated, or the solution-rate gradient becomes steeper, particularly with ordinarily "insoluble" minerals, when the dimensions of the particles are of the orders of magnitude of those

¹ This term is used here to designate any of the clay-like, hydrated, aluminum silicates, whether crystallized like kaolinite, or "amorphous" like clay substance. It is the general group name used by mineralogists.

² See H. Stremme, in Doelter, "Handbuch der Mineralchemie," 1914, II, p. 77.

that make clays.¹ Mellor² has made some experiments along this line on feldspars and micas, with instructive results, as he adopted for his work the treatment used in "rational" analysis. On treatment of a sanidine (orthoclase) with sulphuric acid, for example, he found that only 0.34 per cent was dissolved if the average diameter of grain was 0.165 mm., while 15.64 per cent was dissolved if the average diameter was 0.032 mm.³

Other factors that will seriously influence the results are: the concentration of the reagent, the length of time during which the material is treated, the temperature at which the mixture is treated, and whether this is attained suddenly or gradually or is uniform or varied during the treatment. All of these conditions, and some others, will affect, and generally affect very seriously, the results that are obtained by "rational" analysis.

The various factors enumerated have such an important bearing on the operation of all the modifications of "rational" analysis that its methods are scarcely susceptible of yielding satisfactory duplicate results, except by chance, and even satisfactory duplication of results cannot be regarded as evidence, still less as proof, of their correctness, when the methods are seriously faulty. One can only consider, then, that the methods of "rational" analysis can furnish little but approximate and uncertain, and probably more or less erroneous and misleading, information. It would appear, therefore, that such an analysis is anything but rational.⁴ It would be better to call such an analysis "modal," as it aims at determining the "mode" or mineral composition.

It must furthermore, however regretfully, be pointed out that many writers on, and workers in, ceramics have failed to utilize even the unsatisfactory data of the "rational" analysis with proper understanding of the chemical and mineralogical principles that are involved. Examples of this are numerous in the literature,

¹ It is largely because of this that one must be cautious in applying to clays the data on solubility given in Dana and other text-books; these are rough and are based on particles of much larger size.

² Mellor, "Quant. Anal.," p. 662.

³ See also Langenbeck, "The Chemistry of Pottery," p. 9.

⁴ Cf. Mellor, "Quant. Anal.," p. 674; "Clay and Pottery Industries," p.

and some will be given later, but it may be said here that the application of scientific methods to practical ceramics demands a greater appreciation and understanding of scientific methods than seems now to obtain.

In contrast with the uncertainties of the "rational" analysis, the "ultimate," or what is better called the "chemical," analysis can be carried out with ease and great accuracy by the usual methods for the analysis of silicate rocks.¹ For a clay the usual chemical analysis takes little more time than the rational. Its results, stated in terms of the constituent oxides, may be readily reduced to mineralogical terms by a simple process of calculation that is well known to students of igneous rocks and that will yield information as to the mineral composition of a clay that is far more accurate and certain than the information furnished by the usual "rational" analysis, even when the latter is properly executed and the calculations are correctly made.

It is the chief purpose of this paper to suggest to ceramists this simple and expeditious method of calculating the mineral composition of a mixture of silicates from the chemical analysis, and to describe a modification adapted to the mineralogical characters of clays. The method suggested and to be described is only a special application of the principles and methods of calculation of the so-called "norm" of igneous rocks.² The "norm" is the expression of the chemical composition in terms of certain mineral molecules which are assumed to be, and which, in the great majority of cases, are, actually present in the rock. The actual *mineralogical* composition of a rock is called the "mode," while the rock is classified by the standard *molecular*

¹ W. F. Hillebrand, "The Analysis of Silicate and Carbonate Rocks," *U. S. Geol. Surv. Bull.*, **422** (1916); J. W. Mellor, "Quantitative Inorganic Analysis," **1913**; H. S. Washington, "Manual of the Chemical Analysis of Rocks," **1918**.

² Cross, Iddings, Pirsson and Washington, *J. Geol.*, **10**, 604, 642; also "Quantitative Classification of Igneous Rocks," Chicago, **1903**, pp. 147, 186; G. I. Finlay, "Introduction to the Study of Igneous Rocks," New York, **1913**, pp. 150, 154; J. P. Iddings, "Igneous Rocks," New York, **1909**, I, pp. 419, 433; H. S. Washington, "Chemical Anyalysis of Igneous Rocks," *U. S. Geol. Surv., Prof. Paper*, **99**, 1151-1182 (1917); also separate publication of this portion of *Prof. Paper*, **99**, p. 1918.

composition expressed in the "norm." With clays, in general, the problem and the calculation are much simpler than they are with rocks—since in most clays we have to consider and deal with only three essential minerals, namely, kaolin, quartz, and the feldspars; the micas are of secondary importance and will be taken into account later.

Some of the ideas of the method and some of the data of the calculation have been suggested and used to a limited extent by various writers,¹ and in an interesting paper Staley² has suggested the application of the principles of the norm to the calculation of ceramic mixtures, especially to glazes and enamel mixtures.

Stated briefly, the principle consists in utilizing our knowledge of the various molecules which the constituent oxides are capable of forming, and which they actually do form, and in considering the minerals present in the rock or clay as made up of such molecules, the actual minerals into which the molecules combine being dependent on the conditions and being in accordance with our knowledge of the occurrence of minerals in rocks.

In igneous rocks we are dealing with solidified solutions, during whose solidification and consequent crystallization as a mixture of definite minerals, certain laws of so-called "affinity" of the various basic oxides for silica and alumina come into play and determine the actual mineral composition—which may vary somewhat with the varying conditions that obtain during the solidification.

In clays and similar bodies of secondary origin, on the other hand, we are dealing with the remnants of the alteration, decomposition, and disintegration of these minerals. In these remnants we see not only the effects of the laws just mentioned, but also the action of others which seem to pertain especially to those phases of metamorphism that are known as "alteration" and "weathering," among the products of which are the clays of the potter.

¹ E. g., E. R. Buckley, "Report on the Clays of Wisconsin," p. 1901; C. F. Binns, *Trans. Am. Ceram. Soc.*, **8**, 203 (1906); J. W. Mellor, "Quant. Anal.," pp. 660, 671, 674.

² H. F. Staley, *Trans. Am. Ceram. Soc.*, **13**, 126 (1911); Prof. Staley's suggestion only came to my attention when the present paper had been almost completed.

Let us now consider the example which especially interests us here, and to which we shall confine our attention henceforth: a clay, whether a kaolin, or a porcelain-, ball-, fire-, brick-, stone-ware-clay, or other variety.

The chemical ("ultimate") composition of this is expressed as made up of silica (SiO_2), alumina (Al_2O_3), ferric oxide¹ (Fe_2O_3), magnesia (MgO), lime (CaO), potash (K_2O), soda (Na_2O), water (H_2O), with sometimes small but possibly notable amounts of titanium dioxide (TiO_2) and carbon dioxide (CO_2), and very small and negligible amounts of other constituents.

In mineralogical or "modal"² composition, all clays are essentially mixtures of kaolin = Kl, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$,³ quartz = Q, and the feldspars, orthoclase = Or ($\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$), albite = Ab ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$), and anorthite = An ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$); and, in some clays, small amounts of muscovite = Mu ($\text{K}_2\text{O} \cdot 2\text{H}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$). For the moment, the presence of muscovite and of other minerals will be disregarded, so that the principles may be more readily explained.

The problem before us then is to express the chemical composition of a clay in terms of the minerals kaolinite, quartz and the three feldspars. Their formulas represent the *molecular* composition; thus, kaolinite is made up of one molecule of alumina (Al_2O_3), two of silica (SiO_2), and two of water (H_2O). From the analysis of a mineral the formula is found by reducing the constituents to molecules and finding the ratios of these. We analyse a pure kaolinite and, neglecting the unavoidable slight impurities,

¹ Ferrous oxide (FeO) is not considered here, as it is seldom determined in clay analyses and may be regarded as oxidized to ferric oxide during the burning.

² This term, used to express the actual quantitative mineral composition of a rock, is borrowed from the nomenclature of the Quantitative System of classification of igneous rocks. It corresponds to the "rational" composition of the ceramist, but it must be remarked that the chemical composition is just as rational as the mineralogical.

³ This, the well-established formula of kaolinite, may be taken as that of the clay substance, which is represented by such minerals as kaolinite, halloysite, newtonite, cimolite, and other similar substances of more or less doubtful and possibly heterogeneous composition. They represent the aluminous molecule corresponding to the magnesian serpentine, and differ chemically only in the amount of water content.

we divide the percentage amount of alumina by its molecular weight (102), that of silica by its molecular weight (60) and that of water by its molecular weight (18). It is found that the quotients, which represent the relative amounts of the molecules, are in the ratio 1 : 2 : 2, and consequently we write the formula of kaolinite as $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. The molecular weight of kaolinite is thus $102 + 120 + 36 = 258$; that of quartz is 60, that of orthoclase is 556, that of albite is 524, and that of anorthite is 278.

We have then an analysis of a clay composed "modally," as stated above, and to find its mineral composition from these chemical data we reduce the percentage amounts of the various constituents to molecules by dividing each by its molecular weight; in this case SiO_2 by 60, Al_2O_3 by 102, H_2O by 18, K_2O by 94, Na_2O by 62, and CaO by 56.

Studying the formulas of the minerals under consideration, we see that in each of the feldspars one molecule of K_2O , Na_2O , or CaO is present; Al_2O_3 is present in the three feldspars, and in each in equal ratio (1 : 1) with the K_2O , Na_2O , or CaO , and is present as one molecule as well in kaolinite; SiO_2 is present in all, but in different ratios to the other oxides, making up all of the quartz, being sixfold as much as K_2O , Na_2O , and Al_2O_3 in orthoclase and albite, and twice as much as CaO or Al_2O_3 in anorthite and kaolinite; H_2O is only present in kaolinite, where it is equal to the SiO_2 and twice as much as the Al_2O_3 , and it may also be present, uncombined chemically, as moisture.

The matter now resolves itself into algebra of a very simple sort. For convenience and simplicity, at the start we shall assume that orthoclase ($\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$) is the only feldspar present. To the (molecular) K_2O present we assign an equal (molecular) amount of Al_2O_3 ,¹ and six times the (molecular) amount of SiO_2 , to form the orthoclase molecule. As free alumina does not exist in clays, the rest of the Al_2O_3 must go into kaolinite; so of the SiO_2 we set aside for this mineral molecule an amount out of what

¹ If we take albite and anorthite into account, we should assign, of the Al_2O_3 , amounts equal to those of Na_2O and CaO to form these minerals, respectively, and of the SiO_2 six times that of the Na_2O to form albite and twice that of the CaO to form anorthite.

is left over from the feldspar equal to twice the amount of the residual Al_2O_3 ; we set aside also an equivalent amount of H_2O . This uses up all of the K_2O and Al_2O_3 present, and there is left excess SiO_2 and probably H_2O . The SiO_2 is the quartz molecule, and the excess H_2O represents moisture.

We now have the molecular amounts of the orthoclase, kaolinite, and quartz, and to reduce these to mineral percentages we simply have to reverse the operation of obtaining the molecules; that is, we multiply the molecular amounts by the molecular weights. This can be done by multiplying the molecular amount of each assigned portion of each individual oxide by its proper molecular weight; but it is easier and more expeditious to multiply the molecular weight of each mineral by the figure that expresses the molecular amount of this mineral. This figure is simply the molecular number of that constituent oxide of which only one molecule is present in the mineral. Thus, for kaolinite it would be the molecular amount of Al_2O_3 present in kaolinite, for orthoclase the molecular amount of either K_2O or Al_2O_3 present in orthoclase, and for quartz the molecular amount of the residual SiO_2 . The results of these multiplications will be the mineral or "modal" percentages by weight of the various minerals present, and their sum is the mineral or "modal" composition of the clay.

This process may strike one as very complex and laborious, but it is, in reality, very simple and rapid, particularly after one has had a little practice. Let us take an example, a very simple one to begin with. A clay has the following chemical composition:

	Per cent.	Mol. No.
SiO_2	63.36	63.36 —— = 1.056 60
Al_2O_3	24.28	24.28 —— = 0.238 102
K_2O	3.29	3.29 —— = 0.035 94
H_2O	9.07	9.07 —— = 0.504 18
	100.00	

To calculate the orthoclase first, we multiply its molecular weight, 556, by the unit molecular amount present, 0.035; we have then, $556 \times 0.035 = 19.46 = \text{Or}$. The amount of Al_2O_3 required for orthoclase, 0.035, is subtracted from the total amount, 0.238, and the remainder, 0.203, serves as a measure for the kaolinite. So we multiply the molecular weight of kaolinite, 258, by the unit molecular amount: $258 \times 0.203 = 52.37 = \text{Kl}$, the percentage of kaolinite. All the K_2O and the Al_2O_3 have thus been assigned; the only mineral present now remaining to be calculated is quartz. We therefore subtract from the total molecular amount of SiO_2 , 1.056, the amount used for orthoclase ($6 \times 0.035 = 0.210$) and that used for kaolinite ($2 \times 0.203 = 0.406$), together 0.616; and multiply the remainder, 0.440, by the molecular weight of quartz, 60. We thus have, $60 \times 0.440 = 26.40 = \text{Q}$, as the percentage of quartz. We have now only to consider the water. From the total molecular amount, 0.504, we subtract that which was used for kaolinite, $2 \times 0.203 = 0.406$, and multiply the remainder by the molecular weight of water, 18; the product is the percentage of moisture; thus, $18 \times 0.098 = 1.76 = \text{Aq}$. The mineral composition of the clay is, therefore, as follows:

Kl (kaolinite).....	52.37
Or (orthoclase).....	19.46
Q (quartz).....	26.40
Aq (moisture).....	1.76
	<hr/>
	99.99

This represents the actual mineral composition of such a simple mixture with great exactness, provided of course, the chemical analysis on which it is based is correct; and such a mode is far more accurate and trustworthy than the results of any "rational" analysis made by the often recommended methods.

Let us take a more complex case, in which lime, soda, and ferric oxide are present in addition to the oxides present in the clay just calculated. Suppose that the composition by chemical analysis is:

	Per cent.	Mol. No.
SiO ₂	63.36	1.056
Al ₂ O ₃	23.76	0.233
Fe ₂ O ₃	0.52	0.003
CaO.....	0.69	0.012
Na ₂ O.....	0.97	0.016
K ₂ O.....	1.63	0.017
H ₂ O.....	9.07	0.504
	<hr/> 100.00	

Here (assuming the absence of calcite) the lime (CaO) forms part of residual anorthite, $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, or possibly one of the calcic zeolites, which contain hydrated anorthite molecules. The soda (Na_2O) forms part of residual albite, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$, or possibly may form part of a sodic zeolite, in which hydrated albite or nephelite molecules are present,¹ the difference in silica content of which is of negligible moment. The ferric oxide may be assumed to be present as limonite (Lm), $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$,² the most common of the hydrated ferric oxides. The calculation is briefly done thus: after calculating the orthoclase, albite, and anorthite, the remaining alumina serves as a basis for calculating the kaolinite; the ferric oxide is the basis for calculating limonite; the silica remaining from the orthoclase, albite, anorthite, and kaolinite is the quartz, and the water remaining from kaolinite and limonite is moisture.

The slight deficiency in the summation is caused by the errors in not carrying out the calculations of the molecular numbers beyond the third decimal place, which in this case all tend to low results.

The calculation is represented thus:

¹ The presence of zeolites in clays, and their composition, cannot be discussed here; the lime and soda are present to so small an amount in usable clays that errors in the assumptions above are of negligible consequence.

² This is the formula for limonite as determined by E. Posnjak in an investigation of the hydrated oxides of iron carried out in the Carnegie Geophysical Laboratory, and to be published in the *American Journal of Science*.

$$\text{Or} = 556 \times 0.017 = 9.45$$

$$\text{Ab} = 524 \times 0.016 = 8.33$$

$$\text{An} = 278 \times 0.012 = 3.34$$

$$\text{Kl} = 258 \times 0.188^1 = 48.50$$

$$\text{Lm} = 178 \times 0.003 = 0.53$$

$$\text{Q} = 60 \times 0.458^2 = 27.48$$

$$\text{Aq} = 18 \times 0.125^3 = 2.25$$

 99.88

If carbon dioxide (mol. wt. = 44) is found, it is assumed to be present in calcite (mol. wt. = 100); an equivalent amount of CaO is allotted to the CO₂ for calcite, the calcite is then reckoned by multiplying the molecular number of CO₂ by 100, and the rest of the lime is calculated to anorthite, as above.

Magnesia, MgO (mol. wt. = 40), may be assumed to be present in chlorite, a complex mineral, or rather mineral group, into which biotite usually alters; but it is best treated on the assumption that it enters serpentine, 3MgO.2SiO₂.2H₂O (mol. wt. = 276), the unit of calculation being one-third of the molecular number of the MgO present. Any error involved will be quite negligible.

The micas remain to be considered. Of these, biotite may be disregarded, partly because it is seldom present in more than extremely small amounts in usable clays, and also because, if it is desired to take it into consideration, its amount may, without any practically appreciable error, be assumed to be that of serpentine.

Muscovite is more commonly present, though in small amount. Its composition may be considered as a mixture of orthoclase, alumina and water, so that the percentage amount in a clay cannot be calculated from a chemical analysis alone if orthoclase and kaolinite are present also. However, as orthoclase and muscovite have about the same fluxing effect,⁴ it will serve all practical purposes to calculate the potash of any muscovite

$$^1 0.188 = 0.233 - (0.017 + 0.016 + 0.012).$$

$$^2 0.458 = 1.056 - [(6 \times 0.017) + (6 \times 0.016) + (2 \times 0.012) + (2 \times 0.188)].$$

$$^3 0.125 = 0.504 - [(2 \times 0.188) + 0.003].$$

$$^4 \text{Ries, "Clays," p. 102.}$$

present as orthoclase and the alumina as kaolinite, some of the excess silica being taken for this.

It will be obvious that the separate determination of potash and soda is necessary for the proper calculation of the feldspars. In many analyses of clays, these are not separately determined, but are reported as "alkalies," that is, as the oxides. In the course of analysis the alkalies are weighed together as chlorides, and to calculate these as oxides either the potash and the soda must be determined separately or the chlorides are assumed to be made up in arbitrary (and unknown) proportions of potash and soda. The latter procedure is highly unscientific and unsatisfactory, and it should not be countenanced by workers in ceramics.¹

In order to show the actual results of such calculations as compared with the compositions deduced from "rational" analyses, the calculated norms of several analyses of clays tabulated by Ries,² who also gives their "rational" analyses, are presented in Table I. As, in these analyses, potash and soda have not been determined separately, the calculations have been made on the two assumptions: (1) that the "alkali" is all potash, the alkali feldspar being orthoclase; (2) that it is all soda, the alkali feldspar being then albite. The small amounts of magnesia are disregarded in these calculations.

Several points are clearly evident from a study of these calculated modes as compared with the "rational" analyses; and it is to be remembered that these are only a few of those that have been calculated. It is to be assumed that the chemical analyses are fairly correct, in view of the simplicity of the determinations of the few constituents present.

The first point is that the "rational" analyses do not generally agree with the mode; indeed, some of them are hopelessly and almost ludicrously incongruous. In I, the R. A. ("rational" analysis) while showing about the correct amount of kaolin, gives several times the amount of "feldspar" that could possibly be present on the basis of the alkalies. On the other hand, the R. A. of II

¹ Cf. Washington, *Prof. Paper*, 99, p. 15; Mellor, "Quant. Anal.," p. 222.

² H. Ries, "Clays," 1914, p. 67.

TABLE I.
Analyses.

	I.		II.		III.		VII.		VIII.		IX.		X.	
	Per cent.	Mol. No.	Per cent.	Mol. No.	Per cent.	Mol. No.	Per cent.	Mol. No.	Per cent.	Mol. No.	Per cent.	Mol. No.	Per cent.	Mol. No.
SiO ₂	62.40	1.040	62.52	1.042	63.17	1.053	53.10	0.885	47.60	0.793	46.61	0.777	58.39	0.973
Al ₂ O ₃ ...	26.51	0.260	25.57	0.251	25.09	0.246	33.06	0.324	34.00	0.333	36.47	0.359	27.52	0.270
Fe ₂ O ₃ ...	1.14	0.007	0.92	0.006	0.64	0.004	1.18	0.008	1.30	0.008	2.81	0.018	0.36	0.002
MgO....	0.01	..	0.10	..	0.26	..	0.08	..	0.50	..	None	..	0.41	..
CaO....	0.57	0.010	0.65	0.012	0.35	0.006	0.38	0.007	Trace	..	0.14	0.003	None	..
Alkalies.	0.98	0.010	1.04	0.011	0.80	0.009	0.83	0.009	3.00	0.032	1.44	0.015	4.29	0.046
		0.016	0.017		0.013	0.013		0.013	0.048			0.023		0.069
H ₂ O....	8.80	0.490	9.27	0.515	9.70	0.539	11.32	0.629	13.60	0.756	12.80	0.711	7.19	0.400
	100.41		100.07		100.01		99.95		100.00		100.27		99.68	
Modes.														
Q.....	28.80	27.96	29.76	28.32	31.50	30.54	12.06	11.10	0.00	—3.90	0.06	—1.86	14.94	9.42
Or.....	5.56	...	6.12	..	5.00	..	5.00	..	17.79	..	8.34	..	25.58	..
Ab.....	..	8.38	..	8.91	..	6.81	..	6.81	..	25.15	..	12.05	..	36.15

An.....	2.74	2.74	3.34	3.34	1.67	1.67	1.95	1.95	None	0.83	0.83	7.51	7.51
Kl.....	61.92	60.37	58.82	57.28	59.60	58.57	79.46	78.43	77.66	73.53	87.73	85.66	50.83
Lm.....	1.26	1.26	1.08	1.08	0.72	0.72	1.44	1.44	1.44	1.44	3.24	3.24	0.37
Aq.....	0.05	0.27	0.95	0.77	1.28	1.45	0.09	0.23	2.63	3.20	None	0.52	0.07
	100.33	101.00	100.07	99.70	99.77	99.76	100.00	99.96	99.52	102.32	100.20	102.30	99.30
										3.90		1.86	99.24
										98.42		100.44	

Rational Analyses.

Clay substance	66.33	72.05	67.82	83.39	88.34	96.08	55.88
Quartz.....	15.61	27.78	30.93	14.99	8.95	1.93	5.95
Feldspar.....	18.91	0.10	1.25	1.57	2.73	1.99	38.17

I. Crude kaolin, Webster, N. C.

II. Slip-clay, Lothain, Saxony.

III. Slip-clay, Kaschkau, Germany.

VIII.

White clay, Wiesau, Germany.

VII. Kaolin, West Mills, N. C.

IX. Fire-clay, Bautzen, Germany.

X. Kaolin, Limoges, France.

yields only 0.10 of feldspar although 1.04 per cent of alkalis are present, which demand either about 6 per cent of orthoclase or 9 of albite. The presence of 3.34 of anorthite is also to be considered. Nos. III, VII, VIII, and IX show the same feature. It cannot be objected that the difference is due to adsorbed alkali—since the amount of this would be quite insufficient to account for the discrepancy. No. X shows in its R. A. somewhat high feldspar, but rather of the correct order of magnitude, while the quartz is somewhat too low, and the kaolin too high. It is evident from these results that there is no constant direction of error in the figures of a rational analysis as regards any of the constituents, and that they are therefore quite unreliable and unworthy of use.

The second point brought out is that, in most of the R. A.'s, a very considerable proportion of the feldspar has been dissolved by the treatment with acid and has been reckoned as "Clay Substance." This is clear in II, III, VII, VIII, and IX.

It would also appear that the feldspar is generally almost purely potassic, at least when little lime is present, though it is also evident that the anorthite molecule is present in rather notable amounts in the feldspars of some clays. It is to be remembered that the isomorphous presence of anorthite in the plagioclases increases their solubility in acids. The fact that the feldspars in the clays represented by the above analyses are chiefly orthoclase is indicated in the modal analyses VIII and IX, which show a deficiency in silica. This deficiency is caused by the lesser molecular weight of soda, which takes more silica to form albite than does potash to form orthoclase.

It need only be said, in conclusion, that the utter unreliability of the rational analysis may be considered to be established, and that the term "rational," as applied to this method of determining the mineral composition or mode, is not only a misnomer but contrary to truth.

Attention must also be again called to the fact that, while the suggested method for calculating the mode may appear to be complex and "theoretical," yet it really is simple and expresses very accurately the actual mineral composition. This is so, because of the extremely simple character of the mineral mixture,

the simplicity of the mineral molecules, the impossibility of the entrance of other mineral molecules into the problem to any disturbing extent, and finally the absence of the necessity for considering the molecules of the minerals present as made up of other assumed ones, a difficulty that is met with in the calculation of the modes of igneous rocks when such minerals as aluminous pyroxenes, amphiboles, and micas are present.

This method of calculation is not the only one that might be adopted for arriving at the same results. Thus, without reducing the percentages to molecular numbers, the proportions of kaolin, feldspars, and quartz can be calculated from the percentages directly. Thus the percentage of orthoclase can be calculated from that of potash by multiplying this by 1.085 for the alumina and by 3.832 for the silica, and adding the three figures. The amount of alumina so obtained is to be deducted from the percentage of alumina shown by the analysis, in order to get the basis for kaolin, and the amount of silica is to be deducted from that of the analysis for the balance that goes to quartz and kaolin. The several factors necessary are obtained by calculating the ratios of the different constituents of each mineral to the unit constituent. This will yield the same results as the method described above, but will obviously call for much more numerous calculations. If tables are used the calculations involved in the proposed method are almost entirely done away with.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTION OF WASHINGTON,
August, 1918.

THE ACTION OF ACETIC ACID SOLUTIONS OF DIFFERENT STRENGTHS ON A SHEET STEEL ENAMEL.

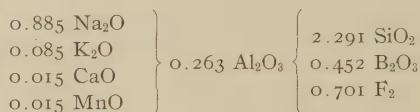
BY LEON J. FROST, Cleveland, Ohio.

For commercial reasons it became desirable to further prove that a 20 per cent acetic acid solution exerts the greatest corrosive action on the type of vitreous enamel generally used on kitchen utensils.

It occurred to us that it might be worth while to place the data resulting from our experiments on record, especially since it bears out so well the work of R. D. Landrum¹ on the same subject.

The procedure was to allow equal volumes of the various strengths of acid to act on the inside surface of small enameled dishes and to determine the loss in weight resulting from this action.

The dishes for this purpose were prepared by coating small basins with, first, a coat of ground and then a thin coat of white enamel. Over these was applied a good coating of the glaze to be tested. The molecular formula of this glaze was as follows:



The enamel frit was milled with 8 per cent of Vallender Clay and 1 per cent of magnesium sulphate. Each dish was marked so as to show the per cent of acid to be used in it and these markings were thoroughly burned in. Only perfect dishes were used so as to minimize any chance of error. The dishes were then carefully cleaned, dried on a hot plate and cooled in a desiccator, after which they were accurately weighed. The required amounts of distilled water and of technically pure acetic acid to make 25 cc. of solution in each case were added from burettes and the

¹ *Trans. Am. Ceram. Soc.*, **14**, 489 (1912).

solutions were taken to dryness on a hot plate, the temperature of which was maintained as uniform as possible. This temperature was such as to cause a slight boiling but not sufficient for any loss from spattering of the solution. Evaporation required about 25 minutes. As soon as the dishes were dry they were removed from the hot plate and, after cooling, were washed and scoured with a soft abrasive so as to remove all material loosened by the action but so as not to affect the enamel itself. After rinsing with distilled water, the dishes were again dried on the hot plate, cooled in the desiccator and weighed.

An attempt was made to keep the conditions of testing as constant as possible. In spite of this care some of the results showed inconsistencies which warranted their being omitted. These inconsistencies were due mostly to chipped rims and pin blisters.

The strengths of the acetic acid solutions used and resulting losses in weight are tabulated as follows:

Per cent acid.	Gr. loss.	Per cent acid.	Gr. loss.	Per cent acid.	Gr. loss.
1.....	0.0056	17	0.0140	50	0.0168
2.....	0.0108	18	0.0151	60	0.0117
3.....	0.0127	20	0.0160	70	0.0076
4.....	0.0140	21	0.0214	80	0.0026
5.....	0.0111	24	0.0223	90	0.0013
7.....	0.0088	27	0.0184	100	0.0003
9.....	0.0127	30	0.0132
15.....	0.0132	40	0.0179

The results are better shown by the curve (Fig. 1). This curve does not check exactly with those presented by Landrum but does show a very similar variation. The fact that there is a marked deflection, greatest at 30 per cent instead of at 25 per cent as reported by Landrum, might be explained by our having used the technically pure instead of the chemically pure acid. There is no apparent explanation for the irregularity between 2 per cent and 9 per cent but from the results of several duplicate trials we are convinced that this was not entirely the result of error.

It is evident from this curve that a 4 per cent to 5 per cent (by volume) solution of such an acetic acid as would probably be

used for testing at most cooking utensil plants is well up in strength as regards its action on the enamel surface. This per cent acid is also of about the same strength as the strongest vinegar—which is probably the most destructive agent to which an enameled

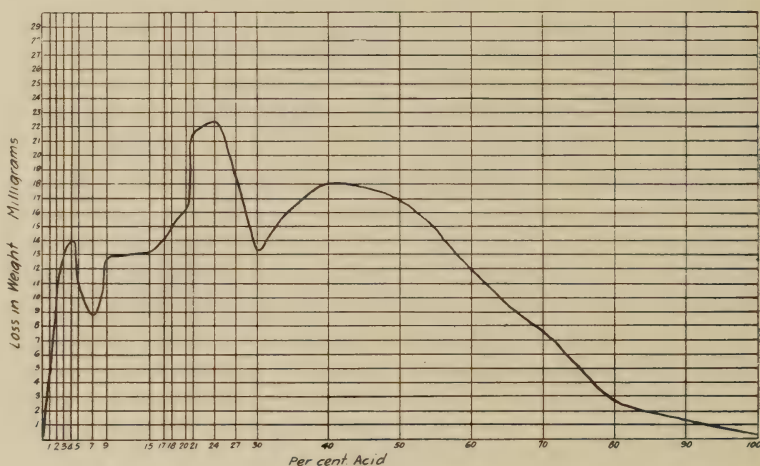


FIG. 1.

cooking utensil is subjected in ordinary use. The high point from 20 per cent to 25 per cent proves satisfactorily the point under investigation.

COMMUNICATED DISCUSSIONS.

J. B. SHAW: It seems to me that this work would have a little more value if the glaze selected for test had been of such a composition as to be less easily attacked by the acid. The glaze used is an alkaline boro-silicate, very high in fluorine, and therefore very soluble in water. While it is similar in its composition to enamels, it would make a very low grade enamel for even cooking utensils and could not be considered for use on ware requiring any special quality as regards acid resistance.

The data obtained seems to prove roughly the original assumption that about 20 to 25 per cent acid is most active on this enamel, but the method of making the test admits so many

possibilities of error that the value of the data is open to question. For instance:

(a) There is no doubt that the strength of the acid varies in every case throughout the period of evaporation.

(b) The rate of evaporation influences the results very materially.

(c) Scouring the surface with abrasives would surely introduce some error.

(d) Loss in weight would be proportional to the surface exposed. The same volume of acid does not necessarily act upon the same area of surface.

It is noted that care was taken to keep conditions constant, but after all precautions have been taken it seems likely that the possible error would exceed the difference between the results obtained with the 4 per cent and 24 per cent acid solutions.

No solvent except water can be maintained constant in a composition during the period of evaporation to dryness. Because of this fact it is impossible to obtain uniformly consistent results in such tests.

I believe a more reliable method of testing solubility—based upon the subjection of a given surface to a solution of constant strength at constant temperature for a short period of time—could be devised.

E. P. POSTE: An interesting feature in connection with the action of acetic acid on enamels came to our attention in the case of a closed unit operating on strong acetic acid at elevated temperatures and under several pounds pressure. An enamel formula, which had been in successful operation in the canning industries under all possible conditions of acidity, and which had also been used on a large number of open units and stills for the stronger acetic acid solutions in various pharmaceutical and chemical manufacturing operations, was specified for this job. The enamel in question failed where the vapors had come in contact with the enamel—but was in perfect condition where it had only been in contact with the liquid. In other words, the action of the acid vapors at elevated temperatures and under pressure was much more severe than that of the liquid. Similar observations have

been made in connection with hydrochloric acid. The volatility of these acids would seem to account for the phenomenon. It has no direct bearing on the action of acetic acid on cooking ware unless it be the possible action of vapors in a covered kettle. However, the lack of pressures under these circumstances would seem to indicate that the case is not parallel.

B. A. RICE: Mr. Frost has very nicely accomplished his purpose and checked previous investigations. It is of interest to note that he secures the same peculiar dip in his curve—just beyond the high point—as did Landrum.¹ The fact that the percentage losses obtained by Mr. Frost are slightly higher is probably accounted for by the fact that he used technically pure instead of chemically pure acid.

Without a doubt the author has chosen the most desirable method of testing the acid resistance of his enamel, that is, by testing the enamel after it is burned on the ware. However, it would have been interesting to have tried checking this curve by subjecting the ground frit to the test outlined by Poste.² Poste compared his acetic acid curve with those obtained by Landrum,¹ but since he was using an enamel of fairly high acid resistance, the high points of the curve were not brought out as clearly as they might have been had a softer enamel, such as is used in cooking ware plants, been used. Should the curves resulting from the testing of an enamel by these two methods be of the same general nature—though the actual gravimetric values would differ—it is quite evident that testing the ground frit would be a much more simple laboratory method of controlling the acid resistance of enamels, once the acid resistance of a standard enamel had been established.

As pointed out by Staley in his discussion of Landrum's article, the method used by the author is accompanied by some very undesirable features: (1) The different rates of evaporation, (2) the variation in the strength of solution—due to evaporation, (3) the constantly changing surface area exposed to the action of the acid. These might be eliminated by simply covering the

¹ *Trans. Am. Ceram. Soc.*, **13**, 494 (1911).

² *Ibid.*, **18**, 137 (1915).

dish with a watch glass and heating at a constant temperature below boiling for a certain length of time. This would allow two means of obtaining results—(1) the loss in weight of the dish, (2) the determination of the amount of dissolved material in the solution. The objection to this method would be the possible effect of the vapors on the enamel. This factor could be reduced to a minimum by filling the dish as full as possible.

It would also be interesting to see the tabulated results of the action of cold solutions on the same enamel after standing a certain length of time. Would a curve plotted from these results be similar to the one obtained with the hot acids?

It might be well to mention also that tartaric acid from cooking grapes, as in making grape marmalade, has a much more severe action on enamels than acetic acid.

The foregoing points will undoubtedly be covered thoroughly by the Sub-committee on Enamels of the Committee on Standards, American Ceramic Society, in its work on the standardization of enameled ware. Some very useful and instructive data will be available for publication by this Committee in the near future.

R. R. DANIELSON: I believe a statement of the number of trials used in each case would throw some light on the irregularities in the data presented by the author. A limited number of trials would undoubtedly cause irregularities—due possibly to such mechanical defects in the preparation of the samples as over-burning, etc., which might not be apparent under casual observation.

I would suggest tests in the interval between 18 and 30 per cent and with variations of 1 per cent. Having this data, it is possible that the author's data might approach more closely the results secured by Landrum and would at the same time make his results more conclusive.

L. J. FROST: Mr. Shaw brings up some very interesting points. It is true that the glaze used was somewhat less acid resistant than the ordinary cooking utensil enamel, but it was chosen purposely on that account so that the variations in the curve would be contrasted the more strongly.

In view of the fact that the same volume of solution was used

in dishes having the same dimensions and the same number of coats of enamel in each case, and that the rate of evaporation was practically the same with every dish tested, I feel that the amount of error introduced here was too small to seriously alter the results. Admitting that the strength of the acid solution does vary in every case, throughout the period of evaporation, it still seems that the action of the acid solutions of different strengths should have the same relation as long as the rate of evaporation does remain practically constant.

A simple method of testing, and one which would give more accurate results in commercial investigations of this nature, would be welcomed by the writer.

The suggestions of Mr. Rice that the curve given be checked by the use of cold solutions, only, for a sufficient period of time, and that this same enamel frit be also tested by the method used by Poste, are very good. The objection to the latter method for control purposes, however, is due to the fact that conditions in sheet steel enameling often necessitate mill additions of so varied a nature as to materially affect the acid resistance of the completed enamel. If the frit alone is tested, this possible variation is lost sight of.

The proposed improvements on the above tests are very worthy of investigation.

Mr. Danielson is correct in his belief that over-burning and other unavoidable conditions of manufacture do cause some irregularity in the results. In running a large number of tests, always with a 20 per cent solution and on the same enamel—which was much more acid resistant than the one given above—I have found 1 to 1.5 mg. loss to be the usual limits of variation. However, when testing two dishes coated from the same lot of enamel and burned at the same time, the results have checked exactly.

NOTE ON COLORS PRODUCED BY THE USE OF SOLUBLE METALLIC SALTS.

BY PAUL G. LARKIN, Denver, Colorado.

Introduction.

For a number of years soluble metallic salts have been used in under-glaze color work. In 1910 experimental work developed that this method could be employed as a means of producing over-glaze color in polychrome terra cotta.

The usual methods of production of polychrome terra cotta involve the painting of colored glazes in the required areas with a camel's hair brush—or the use of shields or stencils to protect certain areas while a colored glaze is sprayed on other portions of the piece. These, and numerous other devices, are objectionable on account of the time consumed, the results obtained, and the uncertainty of the whole process. They are presumably too well known to require further discussion here.

The use of soluble metallic salts offers a partial solution of this problem. By this method the pieces requiring the specified colors are first sprayed with the glaze or slip to be used as a base—the soluble salt solution then being applied to the indicated areas by hand painting. A steady hand and a little judgment are the only requisites for the application. The simplicity of the operation and the rapidity with which the over-glaze solution is applied are decidedly in favor of this method—when compared with the usual operation. To facilitate the application, it is necessary to have a base glaze or slip with an even, smooth surface such as would be obtained at the spray table from a water-glazed piece. A rough or granular-surfaced piece is painted with difficulty and seldom permits of smooth, clean-cut lines. The glaze used should contain a certain amount of gum arabic, molasses, or a similar substance affording a bond of sufficient strength to enable the piece to withstand the handling required during the color application. Generally, standard finish terra cotta is covered with an engobe having a clay content sufficiently high to

give a bond which, with reasonable care, will undergo handling without chipping or rubbing off.

For the past $2\frac{1}{2}$ years this scheme has been used at our plant with good results. It has been used with matt, full-glaze, and standard finish terra cotta. The application on matt glazes, as a whole, gives the best results and the greatest color range—producing colors of cleaner shade than those possessed by either the full-glazed or standard finish ware.

The process is best adapted to color designs in which the area to be treated is comparatively small—particularly if the solution is to be applied by a brush. Uniformity of color may be obtained over large areas by spraying the solution, but this is successful only in the case of flat surfaced pieces—where it would probably be as economical to supply the required color by a glaze containing metallic oxides.

In one instance, a color scheme required twelve colors. The smaller color areas, ten in number, were obtained through the use of soluble salts, while the larger remaining color areas were produced by spraying colored glazes. The colors produced are not entirely free from variation and in a large unbroken area are prone to show unevenness. Nevertheless, the color is generally applied to ornamental pieces and the lights and shadows offset the variations. It is on this last-named type of work that the application of colored glazes gives the greatest difficulty, and, despite the variation obtained through the use of soluble salts, the method produces better results in a shorter time. Ornamental insert pieces, in one, two, or more colors and commercial features, such as name panels and trade marks in color, are easily and quickly manufactured.

Application.

In the application of these color solutions, it is not advisable to use a full brush of the solution as it spreads rapidly and, if applied in this fashion at a point where a clean line is required, gives a blurred outline. The better practice is to use a full brush in the center of a color area and, as the supply of the solution in the brush is depleted, to work smoothly and without undue spreading to the outer edges in order to secure a cleaner line.

One application is sufficient if the surface is thoroughly covered. Solutions that produce a streaked appearance after firing are not improved by a second coating applied in a direction at right angles to the first application. The effect is merely changed from a striped to a checkered one.

Preparation.

The following represents the method employed in the preparation of the different blends:

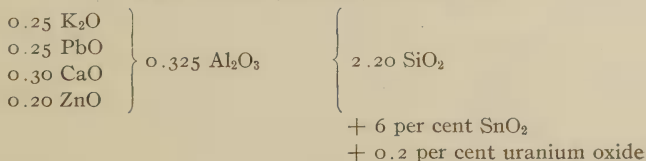
We arbitrarily adopted a standard solvent which consisted of 75 per cent water (not distilled) and 25 per cent glycerine (by volume). Standard solutions of nine soluble metallic salts in this standard solvent were made by adding an arbitrarily adopted weight of each salt to the solvent. A supply of these solutions was kept on hand, in glass-stoppered bottles.

To each standard solution was added 10 cc. of wood alcohol to every 100 cc. solution (or roughly 10 per cent of wood alcohol). The different standard solutions were blended by the use of burettes on a volumetric basis. Aniline dye in solution in alcohol was added to the blends in the same proportion as added to the standard solutions, *i. e.*, 10 cc. aniline-alcohol solution to each 100 cc. of blended solution. For this purpose red, green, blue, violet, yellow, brown and black aniline dyes were used in order to lend color to the solutions and thus aid in the application. This method offers a simple basis for experimental work but does not admit of ready comparison.

FORMULAS—Glazes and Engobe.

The following formulas represent the two types of glazes on which the soluble over-glaze colors were applied:

FULL GLAZE (FRITTED) (CONES 2-3).



MATT GLAZE (Raw Type) (CONES 2-3).

0.060 KNaO	}	0.25 Al ₂ O ₃	}	1.7 SiO ₂
0.073 K ₂ O				
0.032 Na ₂ O				
0.004 MgO				
0.413 CaO				
0.418 ZnO				

The engobe used as the base for the standard finish terra cotta samples had a composition as follows:

STANDARD FINISH ENGOBE (CONES 2-3).

Batch weight. Per cent.	Frit. Per cent.
28.0 Feldspar	75.0 Red lead
23.0 Flint	25.0 Flint
10.0 Cornish stone	
4.5 Frit	100.0
21.0 Ball clay	(Melted down in a frit kiln.)
12.0 Georgia kaolin	
1.5 Borax	
100.0	

Standard Solutions.

The standard solutions used were prepared as follows from technically pure salts:

- | | | |
|--------|---------------------------------------|---|
| No. 1. | 100 cc. solvent. | |
| | 50 g. ferric nitrate. | |
| | 10 per cent wood alcohol (by volume). | |
| No. 2. | 100 cc. solvent. | |
| | 50 g. cobalt chloride. | |
| | 10 per cent wood alcohol. | " |
| No. 3. | 100 cc. solvent. | |
| | 50 g. uranium nitrate. | |
| | 10 per cent wood alcohol. | " |
| No. 4. | 100 cc. solvent. | |
| | 50 g. manganese nitrate. | |
| | 10 per cent wood alcohol. | " |

- No. 5.¹ 100 cc. solvent.
 25 g. chromium nitrate.
 2 g. zinc chloride.
 10 per cent wood alcohol (by volume).
- No. 6. 100 cc. solvent.
 50 g. nickel nitrate.
 10 per cent wood alcohol. “
- No. 7. 100 cc. solvent.
 50 g. copper nitrate.
 10 per cent wood alcohol. “
- No. 8. 100 cc. solvent.
 50 g. tin chloride.
 10 per cent wood alcohol. “
- No. 9. 100 cc. solvent.
 50 g. zinc chloride.
 10 per cent wood alcohol. “

¹ We attempted to use larger amounts of the chromium nitrate in No. 5 but had difficulty in getting it into solution. The difficulty was due to the deterioration of the salt. Zinc chloride was used because a salmon color was desired.

BLENDS FOR GREEN COLORS ON ZINC BEARING GLAZES.

Solution.	No.	$\frac{1}{2}$ C.C.	$\frac{2}{3}$ C.C.	$\frac{3}{4}$ C.C.	$\frac{4}{5}$ C.C.	$\frac{5}{6}$ C.C.	$\frac{6}{7}$ C.C.	$\frac{7}{8}$ C.C.	$\frac{8}{9}$ C.C.	$\frac{9}{10}$ C.C.	$\frac{10}{11}$ C.C.	
Ferric nitrate.....	1					4.5		2.5	8.0	5	4	3
Cobalt chloride...	2	25	20	10	16	17.0	3.0	2.5	2.0	4	5	6
Uranium nitrate...	3	25	22	20	20	19.0	12.5	10.0	10.0	8	8	8
Nickel nitrate....	6			10	5	4.5	9.5	10.0	5.0	8	8	8
Copper nitrate....	7			10								
Manganese nitrate	4		8		9	5.0						
Solvent.....	..						25	25	25	25	25	25

To each blend, 5 cc. of aniline dye in alcohol solution was added.

Each individual blend in the above table produced a green on matt glazes.

Blends Nos. G-4 and G-5 were the best greens obtained and were blue-green on matt glazes and blue on full or bright glazes with a slight green cast. Blue on standard finish ware.

Attempts were made to produce a green, using a combination of solutions No. 7 (copper nitrate), No. 8 (tin chloride), and No. 9 (zinc chloride). The results obtained on matt and full glazes

were not satisfactory. The color in nearly every case varied greatly—blotched in one part with a dark metallic green-black and a light dirty green in another part. Presumably, the base glaze used was not adapted to the production of a copper-green.

Incidentally, green colors were obtained through the use of uranium, but were not stable or dependable and were difficult to combine in harmony with other colors.

BLUE COLORS.

The lighter blues were produced by blending the standard solution of cobalt (solution No. 2) with standard solutions of manganese (No. 4), nickel (No. 6), and iron (No. 1), in varying proportions and in some cases by diluting the cobalt solution.

Blue No. 1:

- 7.5 cc. solution No. 6 (nickel nitrate).
- 2.5 cc. solution No. 1 (iron nitrate).
- 15.0 cc. solution No. 2 (cobalt chloride).
- 25.0 cc. solvent.
- 5.0 cc. aniline dye in alcohol.

Blue No. 2:

- 10 cc. solution No. 2 (cobalt chloride).
- 40 cc. solution No. 4 (manganese nitrate).
- 5 cc. aniline dye in alcohol.

Blue No. 3:

- 15 cc. solution No. 2 (cobalt chloride).
- 15 cc. solution No. 4 (manganese nitrate).
- 5 cc. solution No. 6 (nickel nitrate).
- 10 cc. solution No. 8 (tin chloride).
- 5 cc. solvent.
- 5 cc. aniline dye in alcohol.

Darker blues were produced by increasing the concentration of solution No. 2 (cobalt) by the further addition of cobalt chloride. A good dark blue had the following composition:

Blue No. 4:

- 40 cc. solution No. 2 (cobalt chloride).
- 8 cc. solution No. 4 (manganese nitrate).
- 2 cc. solution No. 1 (ferric nitrate).
- 5 g. cobalt chloride to blend.
- 5 cc. aniline dye in alcohol solution.

BROWN COLORS.

Standard solutions No. 1 (ferric nitrate), No. 3 (uranium nitrate), No. 4 (manganese nitrate), No. 6 (nickel nitrate), and No. 5 (chromium nitrate) were blended to produce brown colors. In general, the efforts were not successful—the colors being light and of a disagreeable shade. The best colors obtained consisted of blends as follows:

Brown No. 1:

- 19.0 cc. solution No. 4 (manganese nitrate).
- 7.5 cc. solution No. 1 (ferric nitrate).
- 11.5 cc. solution No. 6 (nickel nitrate).
- 12.0 cc. solution No. 5 (chromium nitrate).
- 5.0 cc. aniline dye in alcohol.

Brown No. 2:

- 10 cc. solution No. 5 (chromium nitrate).
- 18 cc. solution No. 4 (manganese nitrate).
- 2 cc. solution No. 3 (uranium nitrate).
- 5 cc. aniline dye in solution.

Brown No. 3:

- 30 cc. solution No. 1 (ferric nitrate).
- 10 cc. solution No. 6 (nickel nitrate).
- 10 cc. solution No. 4 (manganese nitrate).
- 5 cc. aniline dye in solution.

GRAY COLORS.

Several acceptable gray colors were produced in blends of solutions No. 1 (ferric nitrate), with a small quantity of solution No. 2 (cobalt chloride), No. 4 (manganese nitrate), and No. 6 (nickel nitrate). A tendency towards brown was noted in the application on full glazes or enamels. The variation is also marked.

Gray No. 1:

- 0.5 cc. No. 2 (cobalt chloride).
- 24.5 cc. No. 6 (nickel nitrate).
- 25.0 cc. No. 4 (manganese nitrate).
- 5.0 cc. aniline dye in alcohol.

Gray No. 3:

- 25.0 cc. No. 1 (ferric nitrate).
- 1.0 cc. No. 2 (cobalt chloride).
- 10.0 cc. No. 4 (manganese nitrate).
- 14.0 cc. No. 6 (nickel nitrate).
- 5.0 cc. aniline dye in alcohol.

YELLOW AND ORANGE COLORS.

The following blends represent the best colors obtained in combining solution No. 1 (ferric nitrate), solution No. 3 (uranium nitrate), solution No. 4 (manganese nitrate), and solution No. 5 (chromium nitrate). The colors are the results of experimental work in an attempt to produce yellow and orange colors

Y-1:

- 20 cc. No. 3 (uranium nitrate).
- 20 cc. No. 4 (manganese nitrate).
- 10 cc. No. 5 (chromium nitrate).
- 5 cc. aniline dye in alcohol.

Y-2:

- 10 cc. No. 1 solution (ferric nitrate).
- 9 cc. No. 3 solution (uranium nitrate).
- 16 cc. No. 4 solution (manganese nitrate).
- 15 cc. No. 5 solution (chromium nitrate).
- 5 cc. aniline dye in alcohol solution.

Y-3:

- 20 cc. No. 3 solution (uranium nitrate).
- 10 cc. No. 4 solution (manganese nitrate).
- 20 cc. No. 5 solution (chromium nitrate).
- 5 cc. aniline dye in alcohol solution.

Y-4:

- 5 cc. No. 1 solution (ferric nitrate).
- 20 cc. No. 3 solution (uranium nitrate).
- 20 cc. No. 5 solution (chromium nitrate).
- 5 cc. solvent.
- 5 cc. aniline dye in alcohol solution.

In attempting to introduce tin chloride as another component in Y-3, we obtained a brown-yellow of unpleasing shade.

The combination of an insoluble stain and a soluble salt gave better results in the production of yellow than the use of soluble salts alone.¹

The following stain was mixed dry, calcined to cones 2-3, wet ground and sieved through a 150-mesh screen:

¹ *Trans. Am. Ceram. Soc.*, 19, 653 (1917).

YELLOW STAIN.

White lead.....	22.6
Antimony oxide.....	20.2
China clay.....	15.8
Tin oxide.....	14.4
Calcium carbonate.....	11.2
Sodium nitrate.....	15.8

 100.0

After calcination at cones 2-3, the stain was dense, brown-yellow in color and rather hard.

This stain, suspended in standard solution No. 3 (uranium nitrate), produced a good orange-yellow color. The blend had the following composition:

Y-8:

35 cc. solution No. 3 (uranium nitrate).

30 g. yellow stain (150 mesh).

35 cc. solvent.

(No aniline dye required.)

Brush application shows variation. The color is good. Further attempts to improve the color by the introduction of 150-mesh rutile produced a lighter color with a brownish cast—not equal to Y-8 in strength. The Y-8 yellow is not as good on full glaze and on standard finish produces a faint yellow with no bond existing between the stain and the engobe.

Comparative Costs.

Some information may be gained on the cost of application of these soluble colors from the following data on a standard finish corner stone and a name panel:

A 40" × 20" rectangular corner stone with 28 V counter-sunk letters required 6½ hours labor at \$0.20 or \$1.30 and materials costing \$0.05, making an approximate total of \$1.35.

The standard finish name panel contained 26 double V-counter-sunk letters with an approximate height of 8". Two colors were applied, one to the outline V and a contrasting color to the deep V or body of the letter. The labor necessary to complete the

color application cost \$1.60 and the materials added \$0.22, making an approximate cost of \$1.82.

Conclusion.

Naturally, there are certain colors whose pyro-chemical requirements cannot be satisfied by a solution application, but as far as this scheme can be carried out, it solves some very perplexing questions in polychrome terra cotta and doubtless can be employed in other fields.

As noted before, it is labor saving; it gives good results; clean lines are a matter of manipulation—except possibly on a full glaze where the color “creeps” during the firing operation (allowance should be made for this movement at the outside edges of the color area).

The addition of a lead frit or flux to a standard-finish engobe—making proper allowance for this addition so as not to bring the engobe to a glaze or semi-glaze condition—will improve to a marked degree the colors produced by the use of soluble salts on standard finish ware.

DENVER TERRA COTTA COMPANY,
DENVER, COLORADO.

NOTE ON THE SINTERING OF MAGNESIA.

By JOHN B. FERGUSON.

Prior to the war, pyrometer tubes, furnace tubes, and similar ware made from magnesia were imported from Germany. This source of supply is now cut off and a new source has not yet appeared. The sintering of chemically pure magnesia has been generally regarded as difficult, if not impossible, and the refractory articles referred to are, in fact, found to contain about two per cent. of forsterite ($2\text{MgO} \cdot \text{SiO}_2$), together with about one per

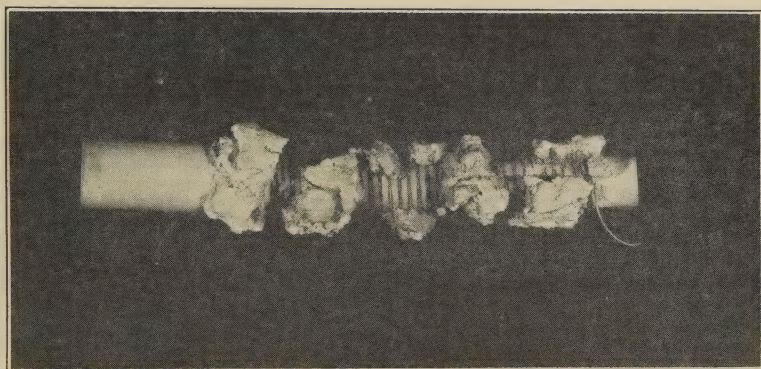


Fig. 1.

cent. of other impurities (estimated roughly under the microscope), which act as a bond. It was thought of interest, therefore, to put upon record some observations on the sintering of silky, calcined, pure magnesia such as is used to insulate small electric furnaces.

In determining the melting points of cristobalite and tridymite,¹ a special electric resistance furnace of the cascade type was employed and the two heaters were insulated from each other by a

¹ J. B. Ferguson and H. E. Merwin, *Am. J. Sci.*, 46, 417 (1918).

layer of silky, calcined, magnesia powder. The furnace was maintained for some hours at temperatures ranging from 1600°C to 1720°C and the magnesia packed so rapidly that it was necessary to add more of it every hour. Upon dismantling the furnace, the magnesia was found to have formed a dense cake surrounding the inner heater, as shown in the accompanying photograph. The cake had considerable mechanical strength. A sintering of this character has not before been observed in our furnaces, which operate usually below 1600°C .

A microscopic examination of this cake by Dr. H. E. Merwin, of this laboratory, did not disclose any binding material; only periclase (crystallized MgO) with less than one-half of one per cent of forsterite ($2\text{MgO} \cdot \text{SiO}_2$) could be identified. The crystals of periclase were interwoven to a considerable extent.

The silica content of the cake was found by chemical analysis to be 0.44 per cent.

The manufacture of magnesia ware of sufficient mechanical strength without a binder would, therefore, appear feasible if the product were fired at temperatures between 1600°C and 1700°C for some hours.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTE OF WASHINGTON,
WASHINGTON, D. C.

AMERICAN CERAMIC SOCIETY.

Acquisition of New Members during September, 1918.

Associate.

Mitsu Kato, Uno Fire Brick Co., Uno-ko, Okayamaken, Japan.	R. B. Gilmore, East Liberty Y. M. C. A. Pittsburgh, Pa.	W. H. Clark, Dow Chemical Co., Midland, Mich.
Olaf Anderson, Statsgeolog, Mineralogisk Museum, Kristiania, Norway.	F. H. Reagan, Locke Insulator Co., Victor, N. Y.	F. A. Harvey, Solvay Process Co., Syracuse, N. Y.
L. Zach Olsson, 130 Pearl St., New York City.	J. S. Brogdon, 701½ Peachtree St., Atlanta, Ga.	Chas. C. Bacon, Ross-Tacony Crucible Co., Tacony, Philadel- phia, Pa.

Contributing.

American Trona Corporation,
724 S. Spring Street,
Los Angeles, Cal.

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* This list is not complete. Information in regard to those who are in some branch of the service and whose names are not included in the above list will be appreciated.

C. F. BINNS, *Secretary*, Alfred, N. Y.

JOURNAL

OF THE

AMERICAN CERAMIC SOCIETY

A monthly journal devoted to the arts and sciences related to the silicate industries.

Vol. 1

July, 1918

No. 7

EDITORIALS.

LOOKING FORWARD.

With the practical ending of the war we look back with pride at the achievements of the Society and its members in the solving of the problems arising in its successful prosecution and in meeting the difficulties arising in the normal conduct of the various branches of the industry. The ceramic industry has kept pace with the advancement of the other great industries during this period of trial and we have seen the successful placing of several new and important products on a firm and lasting manufacturing basis in this country—notably the production of optical glass, chemical glassware, chemical porcelain, etc.

Looking forward, we see some new and some old problems which remain to be faced.

The scarcity and steadily rising cost of fuel of all kinds is stimulating interest on the part of our manufacturers in improved types of kilns and methods of combustion. The suggestion that at our annual meeting in February we have a session at which the merits of the various types of patented dryers, gas-producers, tunnel kilns and continuous kilns be discussed from a technical and economic standpoint, is an excellent one and it is to be hoped that an opportunity for a discussion of this kind will be afforded.

In this number of the JOURNAL, Dr. Ries gives an excellent résumé of the available and prospective sources of high-grade clays in the United States. Linked as it is with the question of the production of high-grade pottery wares from all American

materials, the problem of the location of new deposits of American kaolins and of improvement in the methods of their purification should not cease to receive the attention of our geologists and technologists. We are faced with numerous other problems awaiting attention and solution.

PROFESSIONAL DIVISIONS.

As a culmination of the discussion which has taken place of late in reference to the formation of industrial divisions of the American Ceramic Society, the Board of Trustees has recently affirmed the following motion:

Professional divisions may be formed in the following ways:

1. "When the initiative in the formation of divisions is taken by members who are interested, a petition may be presented by not less than ten members in good standing, of whom three or more shall be Active, who are interested in some phase of ceramic work sufficiently broad to warrant the formation of a special division. This petition shall go to the President who shall then appoint a representative committee to consider the advisability of forming such a division, and to proceed with the organization if the decision is favorable.

2. When the initiative is taken by the Board of Trustees in order to stimulate the growth of the Society, the President shall appoint a representative man to furnish the initiative. He shall select his own committee."

The steady growth and enlargement of the scope of the activities of the Society warrant this action by the Board at this time. Our Society has outgrown the old idea of each member having a broad interest in all kinds of ceramic work. If we are going to maintain solidarity in technical ceramics, as it has been in the past through the American Ceramic Society, we must furnish opportunity for specialization. Professional divisions will furnish this opportunity.

It is to be hoped that there will be no delay in the organization of the respective professional divisions. The problem of the formation of several divisions of the Society at once is not a difficult one and is only a question of which branches of the industry offer the most fertile fields for stimulation and growth. It would appear that the early organization of the glass and pottery divisions is particularly desirable.

In the past the importance of quickening the interest of a larger proportion of the glass industry in the Society has been too little recognized. The technical achievements and awakened interest in this highly important branch of the ceramic industry—through the demands of the war for special glasses—should not be permitted to die out.

It is needless to mention the importance of the active support of the pottery industry to the future welfare and advancement of the Society and the necessity of stimulating research on the problems arising in this basic industry. This is especially vital in view of the ending of the War and the consequent looming up of the old and serious problem of again meeting the competition of the foreign wares.

The organization of professional divisions for the other branches of the industry is of equal importance and in passing we may hastily mention the advisability of the formation of divisions on enamels, refractories, abrasives, etc.

The securing of an adequate supply of professional papers for the issuance of a Journal of even the present modest size has proven somewhat difficult. Through the coöperation of the Professional Divisions and Local Sections there should be an adequate flow of varied technical contributions which will assure the future success of the Society's publications.

ORIGINAL PAPERS AND DISCUSSIONS.

THE OCCURRENCE OF HIGH-GRADE AMERICAN CLAYS, AND THE POSSIBILITIES OF THEIR FURTHER DEVELOPMENT.¹

BY H. RIES.

Introduction.

Although the United States has always ranked foremost among the countries of the world as regards its mineral resources, nevertheless, a not inconsiderable quantity of certain raw materials has been obtained in the past from foreign sources. This was no doubt due in part to the comparative ease and cheapness with which some of these could be obtained, and also to the fact that many of them were of high grade, the result being that domestic consumers in many instances imported certain necessary mineral products rather than search for them in this country.

With the beginning of the great war, certain mineral products, hitherto obtained from central Europe, were almost immediately shut off, while later, owing to the scarcity of ships, it became necessary to further curtail the imports—even of those that could still be imported from neutral or allied countries.

This curtailment of imports has in some respects been beneficial to the United States, for it has stimulated the search for, and development of, good deposits of useful minerals within our boundaries, and it has, moreover, shown the possibility of using low-grade domestic materials hitherto disregarded.

To quote one case outside of the field of clay. For many years we have imported emery from Turkey and Greece. Since

¹ By permission of the Director, U. S. Geological Survey.

the war we have begun the development of a high-grade emery field in Virginia, which apparently contains a large tonnage of this abrasive.

While the clay imports form but a small percentage of the total imports of mineral products, nevertheless, taken by themselves they make up no small tonnage, this in 1916 amounting to 298,866 short tons, valued at \$1,504,233, and in 1917 to 239,318 short tons, valued at \$1,442,059.

The clays which have been imported into the United States include those from central Europe which were used in the manufacture of glass pots, graphite crucibles, enamels, etc., and the china clays and ball clays of England, much sought after by manufacturers of whiteware, electrical porcelain, paper, etc.

While it is true that the supply of the English clays has not been completely shut off, it has recently been diminished on account of dock repairs at Fowey, and still further restricted at a very recent date (August), by an order of the British government—essentially prohibiting the exportation of clay in British bottoms to Boston, New York and Philadelphia.

With the shutting off, therefore, of so much material of value to the ceramic industry, it becomes imperative to determine what means can be, or have been taken in this country to replace imported clays, or what the possibilities are for increasing the output of those high-grade ones now being obtained.

It is, of course, well known that kaolin, ball clays, paper clays, and glass-pot clays have been mined in this country for some time, but nevertheless, they have not fully met the domestic demand in two ways: firstly, there has been an insufficient quantity and secondly, many manufacturers have claimed that, for certain purposes, it was desirable, if not necessary, to include some of the foreign clays in their mixtures—or in special cases to use them exclusively. This, therefore, brings up two problems, *viz.*: first, can the supply of those clays already known and being mined be increased, and second, can we find additional supplies of the types already known in this country, or deposits of new types?

To accomplish this requires two distinct lines of investigation, geologic and technologic.

The geologic investigation serves to show the areas in which new supplies may be looked for, their probable extent, size and, therefore, tonnage. Thus, it saves the prospector and miner much time and money in his search. It also serves to give information regarding the character of the raw materials, their visible impurities, etc.

The technologic study takes up the further development of the problem and attempts to work the newly discovered materials into different mixtures, or possibly find new uses for those deposits of clay already exploited.

It is to the first of these that I shall give especial attention—touching the latter but briefly.

High-Grade Clay Deposits of the United States.

Any one familiar with our sources of raw materials used in the manufacture of the high-grade products mentioned above, knows that most, if not practically all, of them are located in the eastern half of the United States, and while some of value may occur in the far west, they have not been drawn upon by the factories of the eastern and central states—due probably because of the long hauls and consequently the high freight rates.

During the past summer and spring, the writer has had occasion to visit most of the localities in the eastern half of the United States which are capable of supplying raw materials of high grade to the industries already referred to, and in the present paper it is proposed to outline briefly what the chances are for obtaining supplies and also to touch briefly on their present uses.¹

The area under discussion embraces that portion of the United States lying east of the Mississippi and in addition portions of Arkansas and Missouri.

For purposes of convenience of discussion, we may divide this region into several geographic subdivisions as follows:

1. The Atlantic Coastal Plain belt, extending from New Jersey to Florida and Mississippi inclusive.
2. The so-called Embayment Area, reaching from northern Mississippi and Texas northward into southern Illinois and in-

¹ The detailed results of this work will appear in a bulletin of the U. S. Geological Survey.

cluding western Tennessee and Kentucky, southern Illinois, southeastern Missouri, and eastern Arkansas.

3. The Piedmont plateau and mountain belt which lies just west of the Atlantic Coastal Plain belt and extends from Connecticut to northwestern Alabama, and westward to the Appalachian mountains.

4. The Coal Measures region of the central and southern states.

5. The Missouri flint-clay areas.

1. The Atlantic Coastal Plain Belt.—This region is underlain by a series of more or less unconsolidated sands and clays, which dip gently seaward—the most valuable clays having been found almost exclusively in the Cretaceous formation, or oldest one of the series, the only exceptions being certain localities in Georgia and Florida. This means, therefore, that the high-grade clays so necessary to many industries during the war are to be sought for mainly along or towards the inner side of this belt.

In tracing this formation from New York southward to Georgia and westward to Mississippi, we find that it shows considerable variation both as to the character of material and the possible tonnage.

The areas of clay in New York are small and of value chiefly for fire brick, but the extension of this clay belt across New Jersey is well known; indeed, the products of the Woodbridge and neighboring clay pits are so familiar to us as to need no further mention. Continuing to the southward, the same belt crosses Maryland, but shows an entirely different character and is of diminished importance. It is true that along some of the rivers flowing into Chesapeake Bay, such as the Severn, white refractory clays have been reported and do exist, but the deposits are lens shaped and, so far as discovered, are not of large tonnage. There are also, in this same belt, some buff-burning clays of moderate refractoriness which have varied uses in the metallurgical industries, but the individual masses are small and indefinite. The clay from some of these localities is considered adapted for use in the crucible trade.

In Virginia, the Cretaceous formation carries, so far as accessible, no high-grade clays, and the same is true in North Carolina,

but then to the southward, in South Carolina and Georgia, this same formation develops a series of clay beds of striking character and high commercial value. We refer to the deposits of white clays—variously known as kaolins and plastic kaolins. The materials at the present time are widely used in the paper trade and to a lesser extent in the manufacture of whiteware, electrical porcelain and wall tile.

These plastic kaolins are found in certain areas in Bibb, Twiggs, Wilkinson, Washington, Glasscock, Jefferson and Richmond

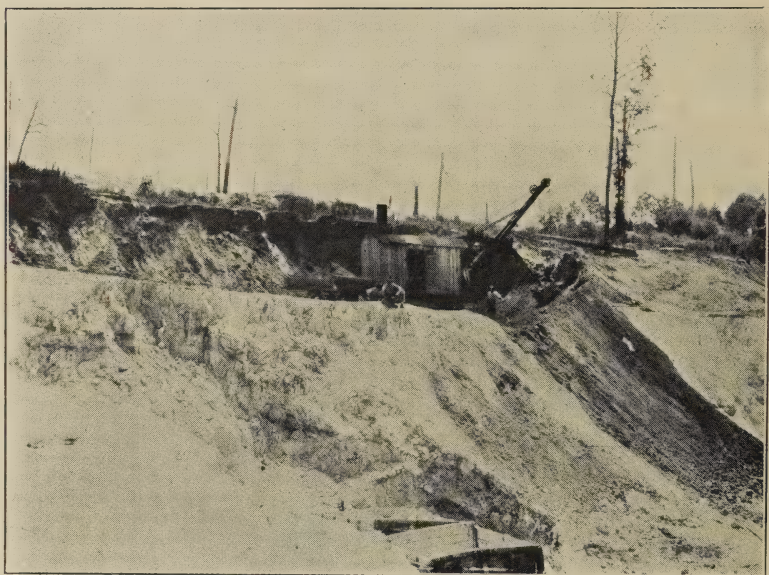


FIG. 1.—Removing sandy overburden from white clay with steam shovel at Gordon, Georgia.

Counties of Georgia; and in Aiken, Edgefield, Lexington, and Kershaw Counties of South Carolina. In Georgia, the clay is worked chiefly in the Dry Branch and McIntyre districts, while in South Carolina, the developments have been chiefly in the Aiken district.

Those of Georgia are usually washed and yield a high percentage of washed product, while those of South Carolina are put on the market mostly in the un-washed but pulverized form.

In view of the widespread demand for these clays, a few words may be said regarding them.

These clays are always in the form of lenses, overlain usually by iron-stained sands. The lenses are of variable size, some of them being large. The overburden of iron-stained sand varies from 3 to 30 feet. The clays are worked at some 15 localities, but there are, no doubt, many other deposits not yet developed, so that the production could be expanded by this means. It



FIG. 2.—Excavating white clay with steam shovel at McIntyre, Georgia.
The overburden is cross-bedded iron-stained sand.

could be still further increased by working the washing plants up to their capacity. This latter would mean a production probably 30 per cent greater than at present. But here we encounter the question of labor supply and transportation facilities—both of which must be improved to aid in further output.

Certain of the deposits in Georgia contain beds of bauxite or bauxitic clay associated with the white clay.

The Cretaceous formation swings around to the westward and is found in Alabama and northeastern Mississippi. There are white clay lenses here, possibly not as extensive as the Georgia and South Carolina ones, and undeveloped. Moreover, they occur in a higher geologic horizon than those of Georgia.

Those in Alabama are found chiefly near Marion, while those of Mississippi are distributed around Iuka, Tishomingo County. The clay lenses in these two states are probably not as large as the

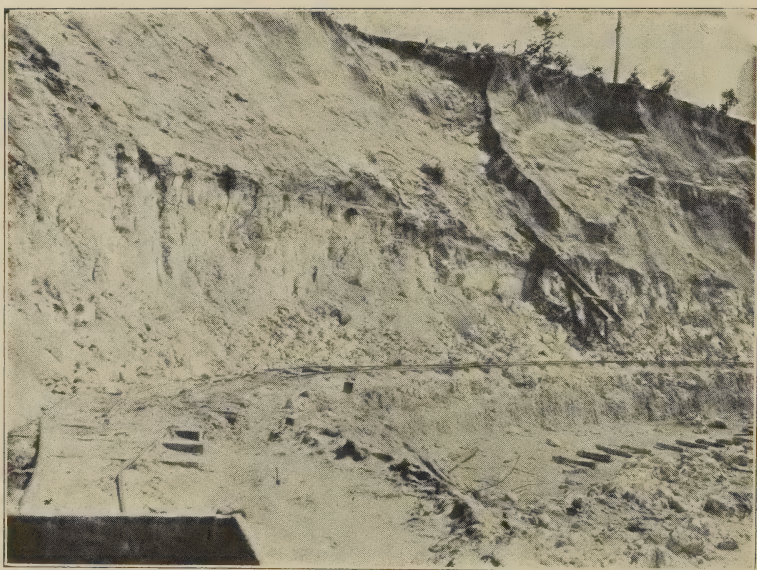


FIG. 3.—White clay overlying bauxite in Sweetwater mine, near Andersonville, Ga. Railroad tracks at upper limit of bauxite. White clay overlain by iron-stained sands.

Georgia and South Carolina ones, nor are the materials always as plastic.

East of the Georgia belt, there are some white clays in the higher lying Tertiary formations, but they have not been utilized. One of the best known overlies the bauxite in the Sweetwater bauxite pit, $5\frac{1}{2}$ miles east of Andersonville, Sumter Co.

There is also the well-known white plastic clay from Florida,

which is worked in Putman and Lake Counties, at points about 60 miles apart, but it probably underlies a considerable area in between and there is a possibility of much greater production.

2. The Embayment Area.—The coastal-plain formations, already referred to, swing northward from northwestern Mississippi and form a belt extending northward up the Mississippi Valley into southern Illinois. The belt also extends for some miles to the east and west of the Mississippi River. It is so-called because

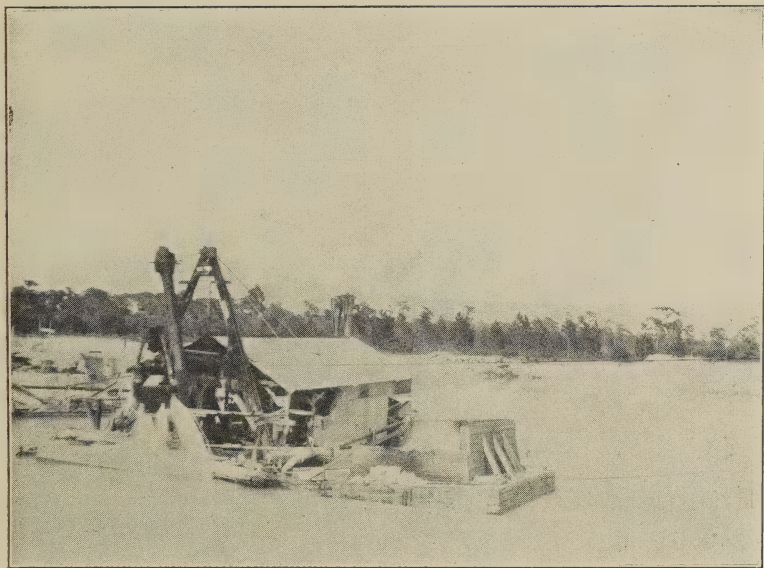


FIG. 4.—Dredging clay at Edgar, Florida.

the Cretaceous and Tertiary formations found here were deposited in a great northward reaching embayment of the sea, and it is here that some of our most important clays are found and where there is, we believe, great possibilities for future development.

Beginning at the south, we have in northern Mississippi several important clay formations which deserve careful investigation, but we cannot speak definitely regarding all of them as yet.

The first of these areas lies in the western half of northern Mississippi—the formation of Tertiary age, known as the Wilcox, containing a great series of white, grayish white, and light pink clays.

If we refer to a geologic section across this portion of the state, we notice that the beds dip westward. Consequently, those of the west half of the area will not be found in the eastern half because they do not exist there—having been eroded—and con-

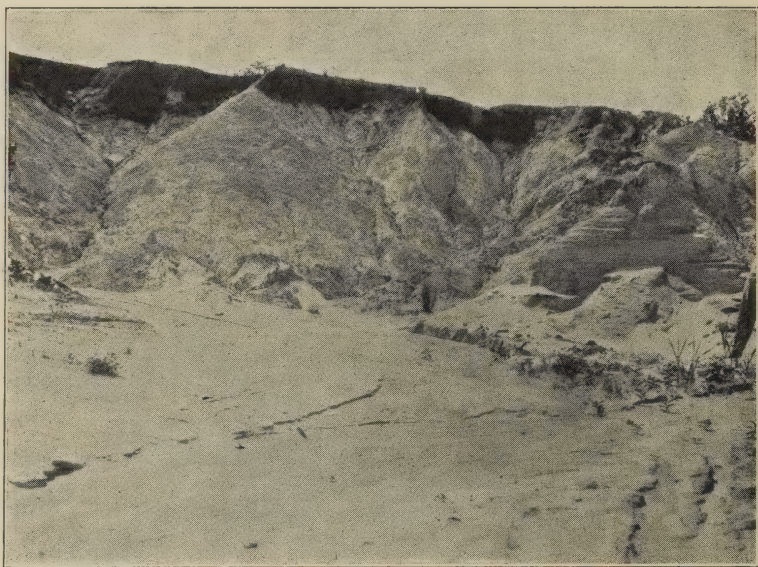


FIG. 5.—Clay pit in Wilcox formation near Holly Springs, Miss. To the right of view the sand rises almost to the surface. At the left of view the clay rises to the surface. This shows the irregular occurrence of the clay in this region. Dark overburden is loam.

versely, those of the eastern half will be found only at considerable depths in the western half.

We separate this area into two halves because the clays are somewhat different. The western half yields clays of tough nature, high plasticity, buff-burning character, dense burning nature, and often high transverse strength. They vary in their

refractoriness. Some are dark colored—due to the presence of finely divided coaly material. The better ones are of the types that can be used in glass-pot mixtures, graphite crucibles, and in the bond of abrasive wheels. Others can be employed in stoneware, etc.

The clays of the eastern half occur in lenses, which sometimes pass rather rapidly into sand beds. The clays themselves frequently show thin layers of sand. They are now used only



FIG. 6.—Pit of refractory bond clay ten miles west of Enid, Miss. The overburden is loam.

for common stoneware, but their value after washing deserves to be considered. The silica content is high, and the iron oxide in published analyses ranges from 1.5 to 4.5 per cent. We question, however, whether we have here a grade of clay as good as those in the western half of the area.

The Tallahatchie county clays, although known for two or three years, are not yet fully developed and we believe that we have here an important clay region for the crucible and glass pot

trade, the demand for which is increasing steadily. The output can be greatly increased by better mining and by better roads and transportation facilities. It is curious that these clays should have remained undeveloped so long, but this may be due to the lack of outcrops, for the clays are usually covered by a sandy loam of varying thickness. However, their white outcrops in the bluffs bordering the Mississippi River bottoms should have attracted attention long ago.



FIG. 7.—Erosion gullies near Huntington, Tenn., showing natural exposure of the light-colored Lagrange clay.

Proceeding northward from Mississippi, through Tennessee and Kentucky, we have the well-known clay belt which has supplied us with ball clays and other grades. The main formation of this belt, known as the Lagrange division of the Tertiary, is really an extension of the Wilcox formation of northwestern Mississippi, but the change in the character of the contained clays is as great as that noted from New Jersey to Maryland. Only in the Southern part of Tennessee, as around Lagrange,

do we find clays approaching the northern Mississippi ones in character. Moreover, within the Lagrange formation, the best clays have been found near its eastern boundary—which extends from the southwestern part of Hardeman County, north-north-eastward through Chester, Madison, Henderson, Carroll and Henry Counties. As we proceed westward, the covering of surface material becomes heavier and the clays will be found only under deeper cover.



FIG. 8.—Digging ball clay near McKenzie, Tenn. Shows the heavy overburden that is removed.

The Lagrange is not the only clay-bearing formation in Tennessee and Kentucky, there being three others forming narrow belts to the east of it, *viz.*, the Porters Creek, Ripley, and Eutaw, but these are, so far as known, of minor importance. No high grade clays have been developed thus far in the western part of the Lagrange area—although ball clay is reported from Eads, Shelby County.

The two questions that are of practical interest are, first, whether the production of these high-grade Tennessee and Kentucky clays can be increased, and second, whether any new uses have been found for them in recent years.

Firstly, as to production. This can be increased by improved labor and transportation facilities—a difficult matter to adjust at the present time. It can also be stimulated by the development of new deposits, which calls for careful prospecting. The



FIG. 9.—Pit of sagger clay near Henry, Tenn. Overlain by orange and white sand.

clays occur in lenses, many of which do not cover more than 10 or 12 acres, but some of which are considerably larger. These lenses are invariably covered by from three to forty feet of sandy overburden, and hence, the clay shows natural exposures only in gullies or stream banks. The fact that another clay lens is known to be near a developed one does not necessarily insure it being of the same quality, indeed, even in any one pit, there may be 7 or 8 different grades of clay.

The indications are that a considerable quantity of undeveloped clay may still remain in this region, but the larger proportion of better grades is probably to be found in the northern half of the Tennessee-Kentucky belt.

With regard to the second point—that of uses—these have expanded considerably since the area was first developed and we may say that they are now used in the manufacture of white-ware bodies, electrical porcelain, glass pots, crucibles, abrasive wheels, enamels, saggers, etc.



FIG. 10.—Pit of ball and sagger clay near India, Tenn. This pit supplies no less than three grades of clay and the overburden is gravelly material.

The same general formation that carries the ball-clays of Kentucky and Tennessee is found west of the Mississippi in Arkansas, but practically no development has gone on there and it affords a good field for the clay miner to prospect in. One exception should be noted, this is near Lester, Ark., where a bed of clay averaging 5 to 6 feet in thickness is found underlying a cannelloid lignite. Tests which have been made of this material

show it to be adapted for use in glass-pot manufacture. There is an excellent chance to develop more clays in this area by further prospecting. Indeed, the formation carrying this clay extends northward in Arkansas and southward into Texas—where the beds of lignite are often underlain by beds of plastic refractory clay.

In the embayment region, there still remains to be mentioned the clays from southern Illinois which lie at the northern end



FIG. 11.—Clay pit at Pryorsburg, Ky., showing no less than four grades of clay in the face of bank. Several other grades underlie the floor of the pit.

of the embayment. These clays have attracted considerable attention in the last few years because of their use in glass pot and crucible manufacture. They belong to the refractory bond-clay type. Mining still continues but it is perhaps a little difficult to forecast the future of the field, since the deposits appear to lie in basins whose exact boundaries do not seem to be definitely known.

3. **The Piedmont and Mountain Belt.**—Lying west of the coastal plain, there is a broad belt extending from western Connecticut southwestward to northeastern Alabama. It is a belt in which new developments are taking place from time to time, but geologically speaking, all of the clays are of the residual type. That is to say, they have been derived from the weathering or breaking down of the rock to clay. These clays vary, then, according to the character of the original rock, which will affect their silica and iron contents.

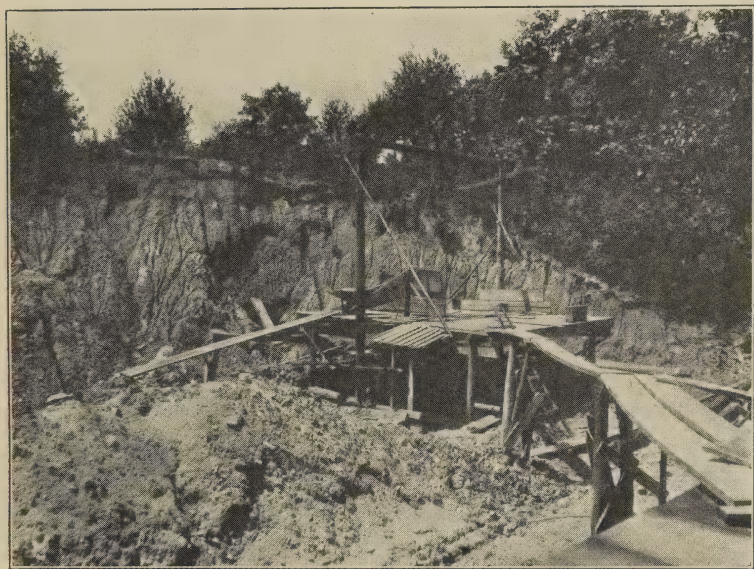


FIG. 12.—Shaft for mining refractory bond clay north of Anna, Ill.

At the northeastern end of the belt, we have a somewhat isolated deposit of kaolin in western Connecticut.

The next region is in southeastern Pennsylvania where kaolins were formerly mined, but the deposits are now exhausted although the extension of the area in Delaware is still worked. No expansion can be looked for here. There are, however, two other districts in Pennsylvania deserving mention, not because they

are new discoveries, but because they contain possibilities. The first of these is a belt passing through Saylorburg, Monroe County, and lying on the northwest side of Chestnut ridge. The clay here underlies the Oriskany sandstone. It has been used crude for portland cement, and in its washed form for paper. Recent developments give promise of its being of use in pottery and the belt should be further prospected.

It is interesting to note that white clays have been discovered in this same formation in northern West Virginia and north-western Virginia, but at present they are not very accessible to transportation.

The second area is in the South Mountain district of Pennsylvania, where the mountain quartzite east and southwest of Mount Holly Springs, Cumberland County, has associated with it white residual clays. The clays are highly siliceous and the silica is very fine grained, so that the product needs careful washing. The crude clay is fairly white, but it does not burn so, so far as tests that have been made would indicate. The output, therefore, may be chiefly of value for paper and paints. Few companies are in operation here and the mining of the clay may present difficulties—due to the treacherous character of the ground—but the region shows possibilities for further development.

Our next area is in Virginia, where we have white residual clays on both sides of the Blue Ridge. Those on the eastern side are similar to the North Carolina ones, to be referred to later, but the Virginia deposits offer little promise—except one in the Nelson Co. district, in the neighborhood of the titanium ore mines.

Those on the western side form a chain of deposits extending southward along the flanks of the Blue Ridge on the eastern side of the Great Valley. They are usually associated with brown iron ore deposits and may be of considerable size. The clays which are derived from the weathering of shales, are white to grayish white when mined, but do not burn pure white in most cases. At present they are worked only at Cold Spring and Buena Vista, but there are other undeveloped deposits between these two points which are worthy of testing. The better grades are of value for paper manufacture and possibly ceramic products.

Considerable attention has been given to the occurrence of kaolin in western North Carolina, northern Georgia, and north-eastern Alabama, where deposits occur, but it is only in the first-named state that the material seems to occur in any quantity, and while the qualities of this material seem to be fairly well known, the supply of future reserves is less in evidence. The present supply could be increased with sufficient coal and labor. Field work carried on in the region this summer shows also that



FIG. 13.—Excavation in white clay near Holly Springs, Pa. The overlying quartzite outcrops at the base of the slope seen in the distance.

the field contains considerable undeveloped material, although some of the deposits are a little remote from the railways.

With the reduction of imports, many questions are asked regarding the possibilities of finding kaolins in other parts of the country. The discoveries up to the present time are few. Indeed, in the northern states, where the soil has been combed off down to bed rock by glacial action, there is little chance of discovering any new ones. The deposits at West Cornwall, Con-

necticut, and St. Remi, Quebec, lying inside the glaciated area, are unique occurrences.

A district of white residual clay, long known but little developed, is in southeastern Missouri around Glen Allen and Lutesville. The deposits may be expected to differ in form from the North Carolina ones because of their slightly different derivation. Those of North Carolina are formed from pegmatite veins and hence are long and narrow. Those of Missouri are derived from lime-



FIG. 14.—Pit in white residual clay near Cold Spring, Va. This clay is residual from Cambrian shale.

stone and hence may be extensive as to the clay mass. More work should be done in this area, but it still remains to be proven whether the deposits of white clay are of large extent. The bodies are irregular in shape and rest on limestone. It is a region of possibilities. The output at one mine is used in plaster board manufacture.

4. The Coal Measures Region.—In our central States, and along the mountains in some of our eastern States, coal fields of great

extent have been developed. Associated with these coals are extensive deposits of shale and clay, many of them being of refractory character and forming the basis of an extensive fire-brick industry, but here and there, refractory clays suitable for glass-pot manufacture have been developed. They are few and far between—the most noteworthy ones being those of the Cheltenham district around St. Louis. Others have been de-



FIG. 15.—General view of flint clay near Owensville, Mo.

veloped at scattered points in Illinois and Ohio, but one cannot help but feel that there is a possibility of finding more.

5. The Missouri Flint Clays.—There remains to be mentioned a peculiar type of clay found in Missouri and commonly referred to as flint clay, but this term hardly tells the whole story.

The deposits of this material are scattered over several counties, notably Gasconade, Franklin, Osage, Warren, etc., in the east-central part of the state. They are very numerous and while many have been opened up, we believe that numerous others

still remain to be found. A peculiarity is their frequent, basin-shaped form—due to the fact that the clay has been laid down in depressions. In these depressions we therefore find this more or less basin-shaped mass of refractory clay, often of the flint type, with its peculiar physical characteristics. Not the least remarkable feature is the mass of granular, öolitic clay, often found within the flint clay, and which runs high in alumina, even up to 75 per cent. This high alumina content is due pre-



FIG. 16.—Mass of diaspore clay in flint clay deposit near Hofflin, Mo.
The rod stands in front of a mass of diaspore clay. The man in foreground is standing on flint clay.

sumably to the mineral diaspore ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$). All of the deposits do not carry the rough clay, as the miners call it, and the quantity present does not seem to stand in any direct relation to the size of the deposit—for the masses may be large or small. The total tonnage visible at the present time is not large, but the total quantity which may be obtained by the continual opening of new pits may be considerable, and so it is a type well worth considering.

Conclusions.

In conclusion, we think it is safe to predict that the outlook for the still greater development of our domestic clays is good—assuming that labor and transportation facilities are available.

We can also assume, we believe, that the reserves in many of the areas referred to are also sufficient for some time to come, and lastly, that this country can supply satisfactory refractory clays of high bonding strength without the use of imported materials. It has also a considerable reserve of kaolins. A single clay may not have all the desired properties, but judicious blending of two or more clays may often yield a mixture having the desired properties.

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THE EFFECT OF CERTAIN IMPURITIES IN CAUSING MILKINESS IN OPTICAL GLASS.

BY C. N. FENNER AND J. B. FERGUSON.

At the time when the staff of the Geophysical Laboratory began to coöperate with the Bausch & Lomb Optical Company in a study of the problems connected with the manufacture of optical glass (that is, in May, 1917) one of the matters which gave much concern, and, for a time, was probably the chief difficulty with which we had to contend, was the rather frequent production of pots of milky or opalescent glass, which was entirely useless for optical purposes.

In endeavoring to locate the source of the trouble and eliminate it, a very puzzling feature was the apparently random manner in which a pot of glass of this character appeared.

Among the four or five standard types of glass which were being produced in large quantities at the time, practically the only one which showed this phenomenon was the "light flint"—a glass which had a PbO content of about 33.5 per cent and whose refractive index was about 1.572.

Although the general procedure as regards the furnace treatment of each pot of this type was practically the same, pots of milky glass appeared in rather large quantities, while at the same time the greater number were perfectly clear.

The samples or proofs which were taken at intervals while the pot was in the furnace never showed any indication of milkiness, and frequently the trouble remained latent or nearly so even up to the time that the cold pot was taken out of the annealing arch, and did not show up until the apparently clear glass was reheated in the muffles for pressing. In fact, it might not be noticed until the pressed glass had come out of the cooling ovens. On the other hand in some instances, after the primary cooling of the pot in the arch the glass appeared milky throughout, or, more frequently, showed a slight opalescence at the top near the

circumference. In all cases in which there was any indication of milkiness reheating increased the turbidity, and even in those instances in which the opalescence appeared at first to affect but a small percentage of glass the whole potful was likely to become milky on reheating.

In endeavoring to obtain light on the matter we learned that this trouble had appeared quite recently, apparently about the time that the use of Russian potash instead of German in the batch had been begun, although information on the latter point was somewhat conflicting.

The German potash, of which there had been an abundant supply before the war and which had been used to the exclusion of potash from other sources, was a very pure material in every respect. The Russian potash contained variable but always considerable percentages of K_2SO_4 and KCl in addition to carbonate. The results of some analyses by Dr. R. H. Lombard of the Geophysical Laboratory are shown in Table I.

TABLE I.—ANALYSES OF RUSSIAN POTASH.

	SO_3 .	Cl.	H_2O .	K_2CO_3 .
1.....	0.75 per cent
2.....	1.9 per cent	7.02 per cent
3.....	...	3.6 per cent
4.....	2.47 per cent	2.03 per cent
5.....	12.2 per cent	3.4 per cent	10.1 per cent	56.1 per cent
6.....	7.7 per cent	3.6 per cent	7.5 per cent	68.7 per cent

In making up the batch about 68 parts by weight of potash (calculated to anhydrous K_2CO_3) to 300 parts of sand were used.

While the cause and prevention of the milkiness were still under discussion, Dr. H. E. Merwin drew our attention to an article which appeared in the *Journal of the Society of Glass Technology*,¹ in which very analogous phenomena were described. Their appearance was attributed to the presence of chlorides and sulphates (especially the latter) in Russian potash, and experiments in confirmation were carried out. Evidence was obtained

¹ J. D. Cauwood and W. E. S. Turner, "The Influence of Small Quantities of Chlorides and Sulphate in Producing Opalescence in Glass," *J. Soc. Glass Tech.*, 1, 187 (May, 1917).

by Cauwood and Turner that a high temperature and extended period of time in heating had beneficial results.

It seemed reasonable to suppose that our phenomena were to be accounted for in the same way, but certain considerations rather obscured matters. First: there did not seem to be any very direct connection between the amount of sulphate or chloride in the potash and the tendency of the glass to become milky. Second: a number of runs were made in an experimental furnace under conditions closely similar to those in the large furnaces. Groups of six small pots holding a few pounds of glass each were placed in the furnace simultaneously. Various amounts of sulphate and chloride were added to the batches. In a given group some pots showed milky glass and others did not, and here again there seemed to be no relation between milkiness and amount of sulphate or chloride added. Third: during a laboratory study of the ternary system CaO-MgO-SiO_2 by one of the present writers (J. B. F.) it had been found that with glasses having compositions within the SiO_2 field, especially with those not so high in SiO_2 as to bring the composition far from the two-phase boundary, a similar milkiness had often been obtained when the crucible was lifted from the furnace (above melting temperature) and quenched in water, especially if the transfer were not carried out very rapidly. At times the depth of milkiness was so great that the glass looked like the so-called Carrara glass. In such instances it had been possible to detect with the microscope multitudes of minute crystals of SiO_2 . This phenomenon could not be ascribed to the presence of chloride or sulphate—as the “ingredients employed were” of a very high degree of purity. Therefore, it was evident that milky glass could arise from other causes.

The opinion toward which we leaned, in view of the evidence, was that sulphate and chloride were probably responsible in some way, but the remedy was not plain. It was not considered practicable to run the furnace temperature much above 1400°C , at which point it was supposed to be held at the time, without running much risk of corrosion and perhaps failure of the pots, nor was it possible to add carbonaceous material to these lead glasses to transform sulphates and chlorides to carbonates.

Nevertheless, before the cause of milkiness was definitely determined, a remedy was found, and later there was a gradual accumulation of evidence as to the cause.

In a previous paper¹ the senior writer has described the work which was done at the Bausch & Lomb plant preliminary to installing a means of temperature-control of a more reliable character than the thermoelements which had formerly been in use. This work showed that the readings given by the thermoelements varied widely from the true reading and, moreover, that the difference was not constant. Therefore, it became evident that the temperature treatment of different pots had been by no means as uniform as supposed. A Leeds and Northrup optical pyrometer was substituted and personal attention was given for several months to keeping the temperatures correct. The furnacemen were instructed in the use of the instrument, so that temperatures at night might be controlled by it, and in most cases dependence could be placed on instructions having been carried out. The result was that from that time forward for a long period there was scarcely a pot of milky glass produced, and when later a few appeared the reason was fairly obvious.

We took special pains to see that the temperature during melting and fining, that is, for a period of about 36 hours, was held at 1400°C or a little higher. The use of Russian potash was abandoned and in its place a much purer material supplied by the Armour Fertilizer Works was used. For the latter material specifications required that the SO_3 content of the potash should not exceed 0.3 per cent and that the Cl should not be in excess of 2.0 per cent. Analyses were made of the contents of each barre supplied and material exceeding these limits was subject to rejection. In general, the furnace temperatures were held at about 1410°C , in order to be on the safe side, and if the SO_3 or Cl content was near the limits considered safe, the temperature was run up to 1420°C . With this increased care and certainty of control, not only was the danger of milky glass al-

¹ C. N. Fenner, "Methods of Temperature-Control in Glass-Melting Furnaces," *Phys. Rev.*, 2nd series, **11**, 2, 141. Abstract of a paper presented at the Rochester meeting of the American Physical Society, Oct., 1917.

most eliminated but also the loss of pots through leakage was very materially lessened.

For some time after the installation of this system, frequent tests were made of the tendency of the glass to become milky by heating small pieces for several hours in clay crucibles to a temperature of $950-1050^{\circ}\text{C}$ in an electrical resistance furnace. It was found that in many instances glass which passed through all ordinary manufacturing processes without any indication of the appearance of milkiness still held sufficient latent possibilities in that direction so that the experimental treatment mentioned developed it to a point where it became visible. Study of the results showed in many cases that this development of opalescence or milkiness could be correlated with the fact that the potash used in the batch contained relatively large amounts of sulphate or that for some reason the furnace temperatures had been allowed to drop below the established point for a considerable length of time.

At a period considerably later than that to which we have been referring it seemed desirable to cut down, if possible, the length of time for which pots remained in the furnace. Apparently as a direct consequence of this change pots of milky glass began to appear again. Whereas under the old schedules a potash containing 0.30 per cent SO_3 could be used without danger and one containing even 0.70 per cent SO_3 could be used without too much risk if the temperature were raised to 1420° or 1430°C , under the new schedule (about nine hours shorter) milkiness appeared when potash containing 0.30 per cent SO_3 was used in the batch. The trouble was much lessened, however, when the length of time of stirring was increased.

All the evidence leads to the inference that the trouble is to be ascribed to the presence of very small amounts of SO_3 and, to a less degree, Cl in the melt. Apparently these substances, when present, are continuously eliminated, but the evolution of the last traces is a very slow process. The elimination is favored by a high temperature and prolonged time, as Cauwood and Turner found, and also by the agitation of the melt which accompanies stirring.

If glass which is milky or is likely to become milky is heated to 1100–1150° C the milkiness disappears, but glass so treated develops numerous bubbles, which render it unfit for use, and a lesser degree of heating does not decrease the milkiness.

Several analyses (made by J. B. F.) show the actual SO₃-content of the glasses. In one case a very milky glass contained 0.14 per cent SO₃. After being cleared up by heat-treatment at 1100° C or a little higher, and having thereby lost its tendency to become milky, the same glass contained 0.06 per cent SO₃.

In another case two lots of glass were made at the same time in the same furnace (a two-pot furnace) and from the same batch. Probably as a result of unequal distribution of temperature in the furnace, one pot became milky and the other did not. The glass from the first pot was found to contain:

SO ₃	0.10 per cent
Cl.....	0.17 per cent

The glass from the second contained:

SO ₃	0.05 per cent
Cl.....	0.17 per cent

Probably in general the presence of Cl in the potash is less serious than the presence of SO₃ when the heat-treatment is similar to that which we followed, but at times enough Cl may be left to strengthen the effect of SO₃ and cause milkiness to appear in a glass which would otherwise remain clear. The last case may be an example of this.

Although the origin of milkiness in glass in the cases described seems to be connected fairly definitely with the presence of SO₃ or Cl, it is doubtful whether the minute particles to which the milkiness is due are themselves composed of sulphates or chlorides. Direct evidence on this point is very difficult to obtain. With the best microscopic magnification it is barely possible to discern discrete particles of foreign matter and nothing can be made out regarding their properties. In fact, the bluish color of the opalescence is itself evidence that the particles are so minute as to be of a similar order of magnitude to the wave-length of light and thus produce a scattering of light rays. According to Wood¹

¹ R. W. Wood, "Physical Optics," 1911, p. 624.

"If a beam of light is passed through a transparent medium containing in suspension small particles, the refractive index of which differs from that of the surrounding medium, light will be given off by the particles in all directions. In the case of particles of the order of magnitude of the light waves, the amount of light scattered increases as the wave-length is decreased, which explains the preponderance of blue always observed in these cases." However, it was found by Mr. H. S. Roberts, of the Geophysical Laboratory, that the size of the particles may be increased by holding a piece of glass of this character at a softening temperature (say 900–1000° C) for several days. Dr. H. E. Merwin examined microscopically the glass so treated and was able to determine that the particles now showed an angular form and possessed a refractive index considerably below that of the glass in which they were imbedded. It seems most probable that the action of the sulphate and chloride impurities is of the sort to which the term "catalytic action" is applied for lack of better knowledge. Ordinary glasses are undoubtedly in a state of unstable chemical equilibrium at the temperature at which the final stages, at least, of the furnace work is carried on. Their stable condition would be one of partial devitrification, and it is an astonishing fact that the unstable state is retained for a prolonged period under conditions of treatment which seem favorable to crystallization. Whatever may be the factors which cause the glassy condition to be retained it appears that the presence of sulphates and chlorides, in quantities so minute that the physical properties should apparently be in no way affected, nevertheless does cause such a change as to permit swarms of sub-microscopic crystals to develop. The phenomena exhibited are of a kind for which very little real explanation can be offered. In geological processes it has long been recognized that the presence of certain volatile constituents, termed mineralizers, is especially favorable to the segregation and crystalline development of minerals in rocks, and the matters here described are apparently of a closely similar nature.

Another occurrence at the Bausch & Lomb plant is of interest in this connection. The light crown glass which was made at the works was never known to be affected with milkiness and it was

supposed that the Russian potash on hand could be employed without detriment in making glass of this type. In a case in which this was attempted the potash contained 6.5 per cent SO_3 , 3.6 per cent Cl and 7.5 per cent H_2O . During melting the impurities separated out and formed a layer of "salt water" on the surface of the glass. At a later stage, during cooling, the glass became so viscous that stirring had to be stopped and the pot withdrawn. When cold the resultant glass was found to contain quantities of nodules or spherulites of devitrified material, whose general diameter was four or five millimeters, although some masses of much larger size were present. Microscopic examination of this material shows that it has a refractive index of about 1.485, very low birefringence, and the typical branching skeleton forms of cristobalite—the high temperature form of silica.¹ A determination by Dr. R. H. Lombard gave a content of 0.28 per cent SO_3 in the glass, and the conditions seemed to be favorable in this instance for the glass to retain the maximum amount of SO_3 possible. The small amount present acted as a very efficient aid to devitrification.

An analysis made by Dr. E. T. Allen on a glass for searchlight mirrors manufactured in England, gave 0.74 per cent SO_3 and 0.10 per cent Cl. The other important constituents were

	Per cent
SiO_2	71.34
CaO	14.73
Na_2O	10.37
K_2O	0.44

This glass showed no indication of milkiness or devitrification. This fact and other evidence given show that the devitrifying effect of sulphate and chloride varies with the composition of the glass.

Although in the cases which have been described the evidence indicates that SO_3 and Cl were responsible for the production of milky glass, it is quite certain that these are not the only substances which are likely to give rise to it. The peculiar "mineralizing" rôle played by SO_3 and Cl is probably filled in some cases

¹ C. N. Fenner, "Stability Relations of the Silica Minerals," *Am. J. Sci.*, [4] 36, 355 (Oct., 1913).

by As_2O_3 or CaF_2 , and there may be other substances having like effect. Also some types of glass (probably quite different in chemical composition from ordinary commercial glasses), such as the CaO-MgO-SiO_2 glasses mentioned on an earlier page, have a tendency toward devitrification in this opalescent or cloudy form, which is apparently inherent in them and does not arise from impurities.

Summary.

In the manufacture of optical glass at the Bausch and Lomb plant, a matter which gave considerable difficulty for a while was the occasional production of pots of glass which were affected by opalescence or milkiness. The evidence indicated that the source of the trouble lay in the sulphate and chloride content of the Russian potash to which recourse was had when the German supply was cut off, although certain facts tended to cast doubt upon this conclusion. It was found, however, that the trouble disappeared when more reliable methods of temperature control were installed, by which an assurance could be had of keeping the temperatures constantly at $1400-1420^\circ \text{C}$, and when the Russian potash was replaced by an American product, more nearly free of impurities. Later, evidence was obtained which connected the milkiness quite definitely with the impurities mentioned, at least as regards the case under discussion, although in other cases the same effect is to be ascribed to other causes.

Reasons are given for the conclusion that the milkiness is caused not by the separation of sulphates or chlorides themselves but to some slight change in the physical properties of the melt which permits the separation of clouds of minute crystals of cristobalite.

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WASHINGTON, D. C.,
September 25, 1918.

SILICA REFRACTORIES.¹

BY DONALD W. ROSS, Pittsburgh, Pa.

Previous Work.

A great deal of work has been done on the stability relations of the silica minerals, the results of which are probably summarized best by Fenner.² More recently, the results of these studies have been applied in the optical examination of silica brick. McDowell³ has been one of the foremost investigators along this line, and at the present time Insley⁴ is conducting an exhaustive study of silica brick made from practically all of the leading varieties of materials used commercially in the United States for this purpose.

The present status of our knowledge along these lines is briefly as follows: The specific gravity of quartz is 2.65, that of cristobalite is 2.33, and that of tridymite, 2.27. Upon heating, alpha-quartz (the stable form at atmospheric temperatures) is inverted to beta-quartz at 575° C. In the presence of a flux, this beta-quartz is transformed into beta-tridymite at 870° C. This, in turn, is transformed at 1470° C into beta-cristobalite—which is the stable form from this temperature to its melting point, 1715° C. "In the absence of a flux, the beta-quartz is transformed directly to cristobalite—which in this case is the final form."⁵ In the manufacture of silica brick two per cent of lime (CaO) is mixed with the quartzite. Upon heating, the lime

¹ By permission of the Director, Bureau of Standards.

² C. N. Fenner, "The Stability Relations of the Silica Minerals," *Am. J. Sci.*, **36**, 331-384 (1913). In this connection it is of interest to note that work recently published by the Geophysical Laboratory of the Carnegie Institution, indicates that the melting point of pure cristobalite is probably 1715° ± 10° C instead of 1625° C as previously reported.

³ J. Spotts McDowell, "A Study of the Silica Refractories," American Institute of Mining Engineers, *Bull.* **119**, p. 1916.

⁴ H. Insley, U. S. Bureau of Standards, Pittsburgh, Pa.

⁵ *Am. J. Sci.*, **36**, 339 (1913).

combines with a small amount of the silica to form a glass, or, in some cases, possibly a little mono-calcium silicate ($\text{CaO} \cdot \text{SiO}_2$). The quartz of a silica brick is transformed first to cristobalite, but as the lime constitutes a small amount of flux, continued heating causes the silica to be slowly converted into tridymite—after approximately two-thirds of it has been transformed into cristobalite.

McDowell¹, Bell,² Le Chatelier³ and others have also studied the differences in finished silica wares due to the use of the different quartzites and to variations in the methods of manufacture.

Usual Method of Manufacture.

Ordinarily, silica brick are manufactured by crushing the quartzite so that it will pass through a 2-inch ring. The crushed material is then fed in batches into wet pans and ground until the largest particles are approximately 0.2 inch in diameter, during which period two per cent by weight of CaO as milk of lime is added along with enough water so that the resulting mix can be molded into bricks. When dry, the bricks are burned in fire-brick kilns of the usual type.

Nature of the Present Work.

Some three years ago, the writer began a study of the silica refractories under the direction of Mr. A. V. Bleining. The present paper is an attempt to set forth a summary of the data obtained since that time and to present some applications of the same. In taking up the data we shall first consider the raw materials, then manufacture and burning, and lastly some of the properties of the burned ware.

Raw Materials.

By far the largest part of the silica brick in all countries are manufactured from quartzites of comparatively early geologic age, although in some cases, chalcedony, chert, quartz sand, or pebbles cemented together with chalcedony, have also been

¹ *Loc. cit.*

² C. E. Nesbitt and M. L. Bell, "Silica Refractories," *Proc. Am. Soc. Testing Materials*, 1917.

³ *Rev. métal.*, June, 1917.

used. Suitable quartzites range from the hard, highly metamorphosed varieties having tightly interlocking grains, to the medium soft rocks which are slightly porous. Loose grained quartzites and sand stones are, however, of little value. The quartzites now being used range from the very young rocks to the oldest sedimentaries.

The following microscopic method may prove of value in judging the suitability of quartzites for the manufacture of silica brick. In the metamorphosis of sandstones to quartzite, the rocks which received but little alteration consist of hard, usually rounded grains of quartz imbedded in a ground mass of a softer material. If a thin section of a rock of this kind is viewed under the microscope, the softer material appears as cloudy areas between the quartz grains. These cloudy areas consist of fragments of silica (probably quartz) and impurities such as hydrated iron oxide. As the metamorphosis proceeded, the interstitial silica, frequently augmented by silica from water solution, crystallized on the larger grains and shows the same orientation as these grains. Silica crystallizing in this way is pure—except for occasional inclusions. Hence, the impurities are segregated. In thin sections of highly metamorphosed quartzites these segregations appear as sharply defined lines between the tightly interlocking, built-up grains of quartz. The quartzites which have been found most satisfactory for the manufacture of silica refractories are those which have moderately to tightly interlocking grains, while those materials which merely show cloudy areas between the harder grains have been found to be less desirable. The specific gravity of quartz is 2.65. The specific gravity of chert rock—although practically the same as that of quartz—is usually slightly below this figure as shown by No. 29 (Table 1) (2.585). This is borne out by Mellor.¹

Screen analyses (by the wet method) and porosity determinations were made on 15 leading varieties of unburned silica brick. These are presented in Table 2, together with the porosities and specific gravities of bricks of the same varieties which have received regular commercial burning.

¹ J. W. Mellor, *Trans. Eng. Ceram. Soc.*, 15.

TABLE 1.

Geological formation from which derived.	Materials. Remarks.	Sample No.	Specific gravity.	Per cent porosity.	Micro-Composition.		
					Quartz plus silicates.	Cristob- alite.	Tridymite.
Medina.....	{ Commercial brick, reheated for 11 days; 4 days at 1450° C and finally 1 day at 1500° C. Commercial brick, reheated 40 times to 1450° C on bag wall of test kiln. Commercial brick, reheated 10 times in commercial silica brick kiln to cone 14. Commercial mix, heated 9 times at successively higher temperatures from 1200°-1500° C by 50° intervals—last 3 heatings were to 1500° C.	33	2.321	29.45	Largely cristobalite and tridymite.		
		34	2.275	31.85	Small amounts of silicates and cristobalite. Rest is tridymite.		
		35	2.271	27.25	11	28	61
		36	2.304	25.19	6	70	24
Baraboo.....	{ Commercial brick which received 9 years' service in Koppers by-product coke oven. Micro-analysis 1 is from the side exposed to heating flue; 2 from center of brick; and 3 from coke chamber side.	37	2.314	19.94	No. { 1 8 2 20 3 3 31 24 }	3	89
						13	67
Homewood.....	Raw rock.	38	2.626	6.52			
		39	2.585	1.83			
Chert from Mitchell limestone, Indiana.	{ Raw rock. Rock calcined rapidly (6 hours) to cone 20. Commercial brick made from chert rock.	40	2.272	14.33			
		29	2.273	25.64	5	12	83
	Commercial German brick, Stella Werke (gives good service).	45	2.372	20.07	20	78	2
	{ Test brick, California quartz + river sand + 2% CaO, 2 heatings in commercial clay brick kiln.	41	2.437	30.02			
	Alabama mica quartz schist rock.	42	2.690	4.52			
	Test brick made from above schist.	43	2.616	34.07			
	{ Test brick made from slightly impure silica sand from Georgia + 8% Ca(OH) ₂ .	44	2.527	30.40			

TABLE 2.
Screen analyses (by the wet method) of raw commercial silica brick mixes. The porosities of the raw and burned bricks and the specific gravities of the burned bricks of the same brands are also shown.

Screen. No. mesh.	No. of brick. % on screen.	MEDINA.						BARABOO.				HOMWOOD FORMATION.	
		6	2	7	3	5	4	18	21	14	16		
		%	%	%	%	%	%	%	%	%	%		
4	..	1.69	2.44	1.43	1.27	9.97	1.41	3.58	1.72	3.25	11.96		
8	..	19.85	24.18	20.22	14.35	15.63	23.46	27.38	20.98	19.09	11.96		
20	..	11.74	9.67	9.15	10.79	10.01	16.07	15.66	17.86	6.09	6.20		
30	..	3.31	6.36	9.15	9.84	7.76	3.75	5.77	8.84	1.89	4.95		
40	..	10.07	9.67	9.69	15.34	17.23	10.93	4.90	7.97	10.22	29.62		
60	..	18.65	13.97	17.13	16.48	12.17	15.02	12.20	5.73	26.35	16.94		
80	..	1.58	5.70	4.99	3.85	2.97	3.60	2.23	4.24	6.29	2.81		
100	..	3.17	4.26	3.76	3.46	3.27	5.68	3.97	3.32	2.07	5.55		
150	..	4.25	3.33	4.10	2.94	2.32	3.91	3.14	2.60	3.87	1.83		
200	..	3.35	2.45	3.07	2.47	1.51	2.90	2.77	2.76	2.55	1.78		
Through 200	..	9.46	6.63	6.25	5.84	2.88	4.39	8.57	11.27	6.89	8.48		
Floated	..	12.84	11.34	11.06	13.37	14.28	8.90	9.84	12.80	11.38	9.89		
Porosity, raw brick	..	26.70	26.15	25.93	27.20	21.22	25.45	23.54	23.20	27.50	28.54		
Porosity, burned brick	..	26.35	25.84	28.35	28.52	22.80	27.16	23.91	23.45	30.58	26.55		
Sp. gr., burned brick	..	2.291	2.295	2.375	2.424	2.340	2.393	2.381	2.390	2.496	2.517		

Screen. No. mesh.	No. of brick. % on screen.	COLORADO.				Mo.	CHERT.	EASTERN PENNA.	Average of all varieties.		Theoretical ¹ for minimum porosity. ¹	Diameter of holes be- tween wires, Inches.
		28	27	31	29							
		%	%	%	%							
4	..	0.23	3.27	0.54	0.37	0.39	2.24	0.40	0.40	0.18		
8	..	14.17	16.18	11.09	15.47	21.76	18.85	28.10	28.10	0.093		
20	..	16.55	22.53	18.15	25.00	22.04	14.52	28.20	28.20	0.034		
30	..	3.25	12.58	9.90	12.14	6.31	7.06	10.30	10.30	0.0198		
40	..	4.09	10.06	9.80	4.77	6.45	10.72	4.40	4.40	0.0150		
60	..	12.05	7.09	11.87	7.55	11.57	13.66	6.10	6.10	0.0087		
80	..	3.62	1.95	3.43	2.37	3.03	3.51	2.50	2.50	0.0068		
100	..	3.08	4.10	4.09	3.93	3.81	3.83	2.50	2.50	0.0055		
150	..	3.92	4.40	3.16	2.78	3.32	3.32	2.25	2.25	0.0041		
200	..	5.04	4.21	3.03	2.48	2.97	2.89	1.75	1.75	0.0029		
Through 200	..	21.32	4.09	9.57	11.44	8.83	8.46	13.50	13.50	..		
Floated	..	12.65	9.53	15.37	11.66	9.53	11.56		
Porosity, raw brick...	..	26.52	22.93	25.30	24.70	20.32		
Porosity, burned brick.	..	24.51	24.63	24.70	25.64	23.10		
Sp. gr., burned brick...	..	2.387	2.393	2.393	2.273	2.480		

¹ Taylor and Thompson, "Concrete, Plain and Reinforced," p. 775. Formula for construction of curve is $d = P^2D/10000$, where

D = Diameter of largest grain.

d = Any given diameter.

P = The per cent of mixture smaller than any given diameter.

Largest grain = 0.182 inch diameter.

Curves showing the results of screen analyses made on quartzites that have been crushed ready to be molded into brick, when compared with the theoretical curve for minimum pore space,¹ show that there is always an excess of material of the sizes which correspond to those of the quartz grains.

In crushing, sandstones and quartzites that are but slightly metamorphosed break mostly to individual sand grains and yield an excess of these sizes.

Moderately metamorphosed material, *i. e.*, material that is still slightly porous, follows the theoretical curve quite closely. In this case the breaking is usually through the interstitial material between the built-up grains. However, the interstitial material breaks free from some of the original rounded grains and still other grains are broken in two.

In the case of highly metamorphosed quartzites, *i. e.*, those in which the crystalline quartz is practically continuous, the breaking is usually through the grains, but a fair percentage of rounded grains also break free from the interstitial material. This breaking away of the interstitial material from the rounded grains is particularly noticeable in the highly metamorphosed Baraboo quartzites.

Inspection of the screened material revealed the fact that in the Medina, Baraboo, Homewood, Missouri, and Eastern Pennsylvania materials, the original rounded grains which broke free from the interstitial material practically all passed through a 30-mesh (0.503 mm. diam.) screen, and that but very few particles passed through a 60-mesh (0.221 mm. diam.) screen—the great majority being caught on the 40-mesh (0.381 mm. diam.) and 60-mesh screens, in varying proportions. In Fig. 1 are shown photographs of samples of material remaining on the 40-mesh screen. No. 6 consists largely of material broken through the interstitial material between the built-up grains, and some that has broken through the grains. A slight amount of finely ground material still adheres to the particles. No. 21 shows a large percentage of the original rounded grains which have broken free from the material of the built-up grains. No. 12 contains a large percentage of material broken through the grains and

¹ Taylor and Thompson, "Concrete, Plain and Reinforced," p. 775.

also material in which the breaking was between the original rounded grains and built-up grains. A slight amount of finely ground material still adheres to the particles. In No. 14, the original grains of the material appear more angular than is the case with the other quartzites examined. In No. 31, many

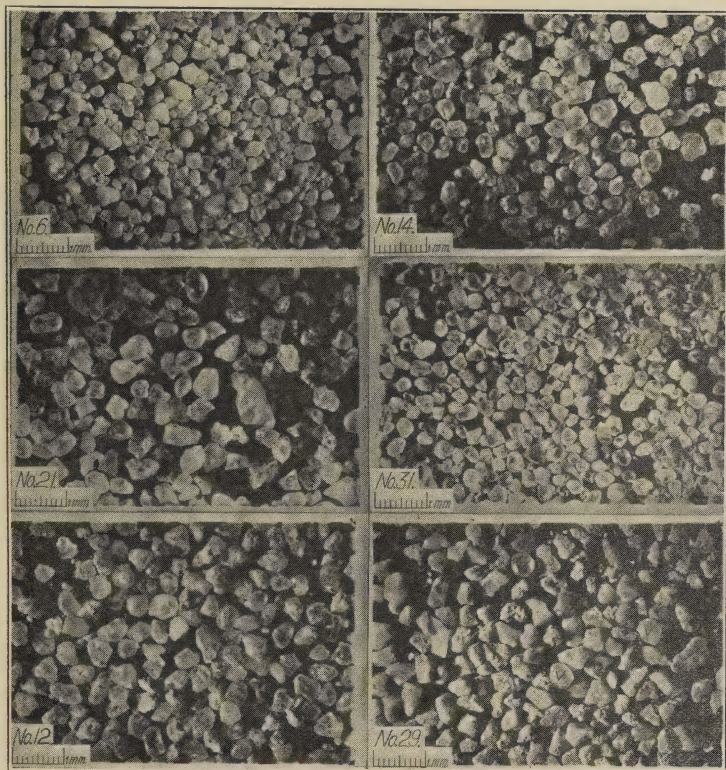


FIG. 1.—Materials (caught on 40-mesh sieve) resulting from wet screen analyses of raw commercial silica brick mixes. Magnified.

(Microphotographs by Dr. R. Thiessen, U. S. Bureau of Mines, Pittsburgh, Pa.)

of the original rounded grains have broken free from the chalcedony bonding material. In No. 29, the grains in the chert are extremely fine, hence, as might be expected, it breaks into angular fragments. A slight amount of finely ground material

still adheres to the particles. The three grains checked are of a different material which was accidentally included.

At the present time, McDowell is carrying on a study of the sizes of the built-up interlocking grains of several quartzites.

Of the quartzites, the loosely bonded varieties yield the most porous raw brick, and the strongly bonded varieties, in which the breaking is across the grains—thus avoiding an excess of material corresponding to the grain sizes—yield raw brick of the least porosity. Material No. 12 (Table 2) is of this type and has the lowest porosity of any of the unburned brick tested. The chert material, No. 29, is next, this being closely followed by the mixes made from Baraboo quartzite, while the large majority of the raw mixes made from the Medina quartzite, of Blair and Huntingdon counties, Pennsylvania, show in turn somewhat greater porosities than do the Baraboo materials.

Innovations in Methods of Manufacture.

Finished silica brick frequently show quite wide variations in their physical properties when subjected to strength tests, etc. These variations may be due in part to differences in grind from one pan to the next, and, in part, to the human factor in hand molding. To overcome such difficulties in special cases, the following changes in the methods of manufacture have been suggested:

The material is ground and, by screening, is divided into three sizes. These are then mixed in the desired proportions in a machine similar to that used for mixing concrete. To avoid storage in bins,¹ the material might be ground directly in a wet pan having raised mullers. The lime is added at this point. The brick are then machine molded. This should insure greater uniformity of texture, shape, amount of material per brick, and should tend to slightly reduce the porosity. Nesbitt and Bell²

¹ When crushed materials are poured from a spout into a bin there is a tendency for the coarse material to segregate from the fines. This trouble may be largely obviated by frequently changing the position of the spout while a bin is being filled. It is essential to keep this in mind when using bins for the storage of ground silica brick materials.

² *Loc. cit.*

have suggested that 1500 pounds per square inch is the most desirable pressure for use in the manufacture of machine molded silica brick. Fine surface cracks appear to be characteristic of machine-pressed silica brick. However, in most cases these should be of no serious detriment to the bricks. In making silica brick by machine, the water content need not be quite so great as for the hand-made brick. However, an abnormally low water content is apt to result in an open brick of weak structure—both in the raw and burned condition.

Effects Produced by Burning.

Since the specific gravities of cristobalite (2.33) and tridymite (2.27) are considerably lower than that of quartz (2.65), the relative position of the specific gravity of any sample of silica brick between these limits should indicate, quite accurately, the degree to which its quartz has been transformed to the lower specific-gravity forms.

To accurately determine the specific gravities of solids by means of a pycnometer bottle, using finely powdered material, is a rather tedious operation. Hence, an effort was made to determine the specific gravity by using a two-inch cube of the material. This was first weighed dry, then saturated with water and weighed wet, and finally the saturated piece was weighed, suspended in water. From these data, the specific gravity was calculated. Saturation was obtained by placing the pieces in boiling water and subjecting them, while thus submerged, to a vacuum equivalent to twenty-four inches of mercury for a period of four hours. This method, when carefully conducted, has been found to give the specific gravities with sufficient accuracy for our present purpose.

The specific gravities of most of the leading varieties of commercial silica brick, manufactured in the United States, have been determined in this way (see Table 3) and, thus far, all lie between 2.65 (the specific gravity of quartz) and 2.27 (the specific gravity of tridymite). The results of our own work, and more recently of that of other investigators of silica refractories, indicate that this gives a definite and satisfactory indication of the degree to which a brick has been burned.

TABLE 3.—POROSITIES AND SPECIFIC GRAVITIES OF PRINCIPAL BRANDS OF COMMERCIAL SILICA BRICK MADE IN THE UNITED STATES.

Quartzite from which the brick were made.	Sample No.	Specific gravity.	Per cent porosity.
Medina (Tuscarora).....	1	2.375	27.15
	2	2.296	25.84
	3	2.424	28.52
	4	2.393	27.16
	5	2.340	22.80
	6	2.291	26.35
	7	2.375	28.35
	8	2.336	31.52
	9	2.321	25.97
	10	2.358	26.10
	11	2.291	29.56
	12	2.480	23.10
	13	2.340	29.88
		Av., 2.357	Av., 27.07
Homewood sandstone.....	14	2.496	30.58
	15	2.448	28.95
	16	2.517	26.55
		Av., 2.470	Av., 28.69
Oneida.....	17	2.274	25.66
Baraboo.....	18	2.381	23.91
	19	2.430	25.15
	20*	2.325	31.41
	21	2.390	23.45
	22	2.395	24.79
		Av., 2.399	Av., 24.30
Quadrant formation (Montana).....	23	2.495	23.22
	24	2.490	22.66
	25	2.537	22.96
Alabama, probably Weisner formation.	26	2.311	29.75
Dakota and Comanchian (Colorado)...	27	2.393	24.63
	28	2.387	24.51
Indiana chert.....	29	2.273	25.64
Saint Louis district.....	30	2.363	25.73
	31	2.393	24.70
Eastern Pennsylvania.....	32	2.335	26.85
Grand average of all varieties.....	Av., 2.384		Av., 26.34

* Calcined quartzite.

Using the specific gravities of the materials in this way, our data (Table 4 and Fig. 2) indicate that at the end of heating to 1500° C (conducted as follows: heating to 800° C in 18 hours, heating from 800° C to 1500° C in 6 hours, and held at 1500° C

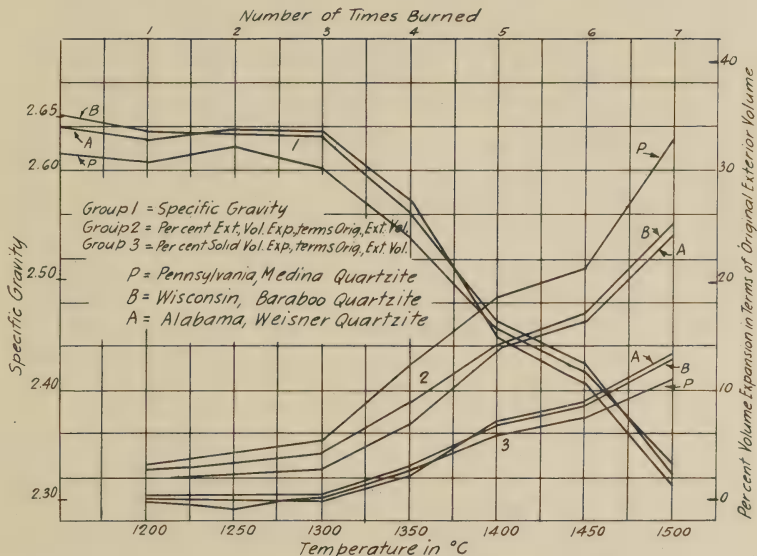


FIG. 2.—Changes in exterior and solid volumes and specific gravities of Medina, Baraboo and Alabama quartzites, caused by repeated burnings to successively higher temperatures from 1200°–1500° C.

for 1½ hours) the amount of transformation that had taken place was approximately the same in the Baraboo, Alabama, and Medina quartzites. The specific-gravity curves show that, for the repeated heatings at from 1300° to 1400° C, the Medina quartzite appears to be transformed slightly more than the other two. The average specific gravity (Table 3) of commercial brick made from the Baraboo quartzite is somewhat higher than that of brick made from the Medina quartzite. Hence, since the chief part of the burning received by average commercial brick is between 1300° and 1400° C, it is probable that at these temperatures Baraboo quartzite is actually transformed at a slightly slower rate than is the Medina

TABLE 4.—SPECIFIC GRAVITIES OF QUARTZITES BEFORE AND AFTER HEATING FOR $1\frac{1}{2}$ HOURS AT 1500°C .

Material.	Specific gravity. Raw quartzite.	Specific gravity of quartz- ite after 1500°C burn.
Medina quartzite.....	2.635	2.303
Baraboo quartzite.....	2.650	2.293
Alabama quartzite.....	2.640	2.295
Homewood sandstone.....	2.630	2.326
Montana quartzite.....	2.638	2.306

quartzite. When quartz is transformed to cristobalite, the action is progressively from the surface and along cracks towards the interior and hence is most rapid in the varieties having the greatest surface areas. In accordance with this we would expect the slightly porous Medina quartzite to be transformed somewhat more rapidly than the more highly metamorphosed, non-porous, Baraboo quartzite. At temperatures above 1400°C , however, the transformation of quartz to the lower specific-gravity forms is so rapid in all varieties that the above effect is apparently obscured.

In silica brick, the transformation from cristobalite to tridymite apparently takes place first in the fine material of the ground mass and then progressively from the surfaces to the centers of the larger particles. This is illustrated in Fig. 3, which shows a

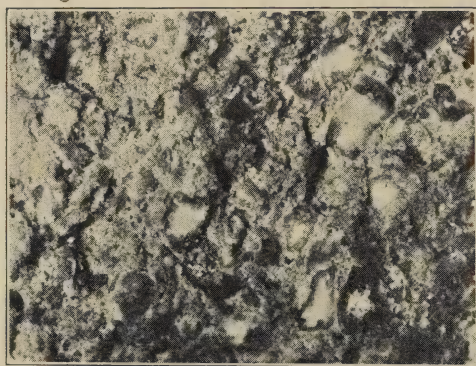


FIG. 3.—Brick made from Medina quartzite, after 40 heatings to 1450°C . Ground mass is tridymite, gray outer portion of large particles is tridymite in glass, and white centers of large particles are cristobalite (natural size).

fractured surface of a brick which has been burned to an advanced stage. In this case the quartz has almost entirely disappeared and practically all of the cristobalite that remains is represented by the light patches present at the centers of the larger particles. In the course of the transformation of quartz through cristobalite to tridymite, the original crystal form is largely lost, so that the final product shows a considerable quantity of interlocking crystals which were not present in the unburned brick.

In accordance with Mellor,¹ we found that chert is transformed to the lower specific-gravity forms much more rapidly than quartz. Thus, brick 29 (Table 3) (micro-analyses shown in Table 1), which was made from a chert rock, received one regular burn in a commercial silica brick kiln. Its specific gravity is lower and the sum of its contents of cristobalite and tridymite is much higher than is usually the case with single burn bricks made from quartzite.

A comparison of the porosities of raw and burned brick (Table 2) shows that the porosity of the burned brick depends largely upon the porosity of the raw mix. However, it was found, by repeated trials, that if a raw brick mix was heated to 1500° C in one day the resultant product was porous, weak and friable, while if fourteen days were consumed in reaching the same maximum temperature, with a protracted soaking at from 1200° to 1350° C, the resultant brick showed no undue increase in porosity and was sound and strong. In fact, in cases where the conversion of quartz has been practically completed at the soaking temperatures, the final increasing of the temperature to the maximum actually causes the porosity of the brick to decrease. As a rule, the increased porosity (puckiness) of rapidly burned brick is much more pronounced with loosely than with firmly bonded quartzites.

Number 37 (Table 1) represents a piece of brick which received long soaking in use in a by-product coke oven at moderately high temperatures. The differences in micro-composition from the hot (heating flue) side of the brick to the cold (coking chamber) side are very marked. For the specific gravity and porosity determinations, pieces were taken which extended entirely across

¹ *Loc. cit.*

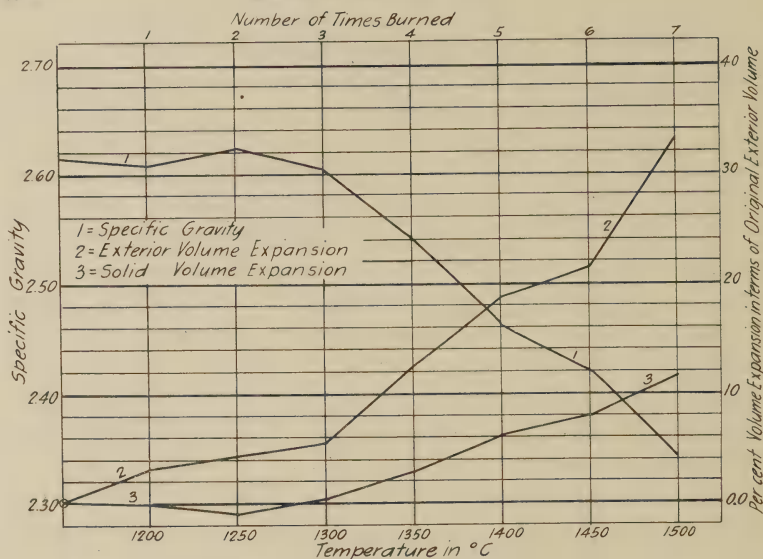


FIG. 4.—Changes in exterior and solid volume and specific gravity of Medina quartzite, caused by repeated burnings to successively higher temperatures from 1200°–1500° C.

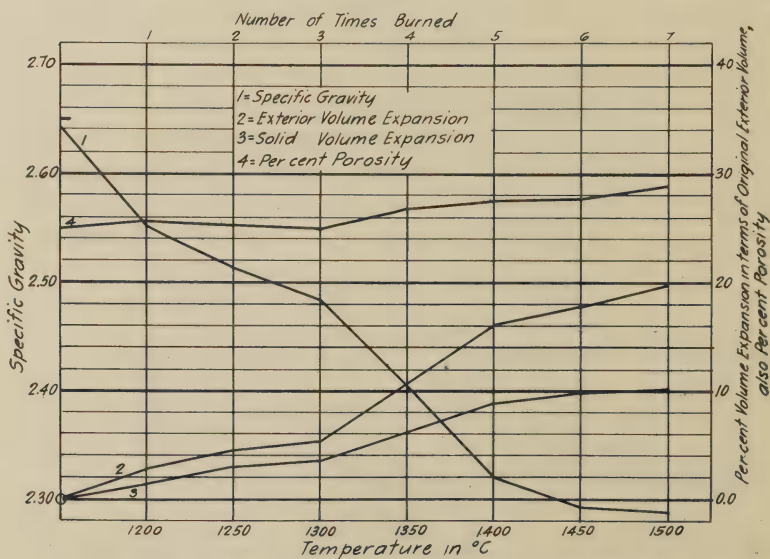


FIG. 5.—Changes in exterior and solid volume, specific gravity and porosity of Medina raw mix—caused by repeated burnings to successively higher temperatures from 1200°–1500° C.

a section of this brick. The abnormally low porosity of this brick was in all probability caused by the protracted soaking at high temperatures which it received in use. This brick is of particular interest because of its low cristobalite content, even at the coke side—where there is considerable quartz + silicates present.

A comparison of the specific-gravity curves in Figs. 4 and 5 indicates the way in which the lime increases the amount of transformation produced by a given heat treatment. Increasing the lime content above two per cent appears to further increase the rate of transformation. Sodium chloride apparently has a similar effect. On the other hand, plastic clay, pure calcined alumina (ground to pass through a 60-mesh screen), and iron oxide appear to have very little effect on the rate of transformation. Small percentages of fluorspar (CaF_2) were tried in conjunction with lime, and although our data is not conclusive, the indications are that the fluorspar has very little effect on the rate of transformation.

Properties of the Burned Brick.

The results of cold cross breaking tests (Table 5),¹ in conjunction with the natures of the materials broken, and their specific gravities, porosities (Table 3), micro-analyses, etc., indicate that, with brick made from quartzites, the strength of slightly to moderately burned brick probably depends largely upon the

TABLE 5.—CROSS BREAKING TESTS. (MODULUS OF RUPTURE.)

Test No.	Material.				
	(18) Baraboo.	(6) Medina.	W. Va.	(29) Chert.	Medina. ²
1.....	565	1557	664	446	...
2.....	593	709	1143
3.....	544	452	782
4.....	546	1003	645
5.....	527	863	809
Av.....	555	915	809	...	793

¹ Bricks set on edge with six inches between supports.

² As given by McDowell.

state of metamorphosis of the raw material and the porosity of the raw brick and the lime-silica bond formed in the burning. On the other hand, well burned silica brick appear to have their strength somewhat increased by the formation of interlocking crystals—occasioned by the transformation of the quartz to the lower specific-gravity forms. Seaver¹ likewise maintained that the interlocking crystals of well-burned silica bricks increases their strength.

If all other properties of a silica brick made from quartzite are found satisfactory, it is not usually found that the brick will fail in use because of lack of strength. The Baraboo and Medina varieties (Table 5) have both been thoroughly tried out in steel furnace and coke oven work and both give consistently satisfactory results. The great variations in strength of the Medina brick, as compared with the Baraboo, may be due to an unequal development of interlocking crystals in the individual specimens of the former.

In Table 6 is presented the data of crushing tests made upon "Star" silica brick at various temperatures as reported by

TABLE 6.—CRUSHING STRENGTH OF SILICA BRICK AT VARIOUS TEMPERATURES (LE CHATELIER).

Temperature ° C.	Crushing strength of hot brick.	
	Kg./sq. cm.	Lbs./sq. in.
15	170	2418
520	158	2247
670	150	2133
800	139	1977
950	125	1778
1050	120	1707
1200	85	1209
1320	62	882
1460	50	711
1540	37	526
1600	30	427
1700	12	171 ²

¹ K. Seaver, "Manufacture and Tests of Silica Brick for the By-Product Coke Oven," *Trans. Am. Inst. Mining Eng.*, **53**, 125-139 (1916).

² Extrapolated.

Le Chatelier.¹ The 1700° C figure has been extrapolated by a continuation of the curve. This curve would seem to indicate that hot crushing tests, to be of the most value, should be made at a temperature that corresponds to the working conditions—such as the temperatures of the crowns of steel furnaces. Or, if made at any other temperature, the strength obtained should be compared to that at the corresponding temperatures on previously prepared curves of the above nature. Such prepared curves should of course include varieties of materials similar to those under test.

McDowell,¹ in his tests of silica brick which had been burned from one to ten times in a commercial kiln, found that at the end of the first few burns the strength had reached a maximum—after which it declined slightly. His theory is that this decrease is due to a slight rupture of the brick—caused by repeated heating and cooling—rather than to an inherent weakness of one or both of the low specific-gravity forms of silica.

In making load tests on silica brick, it was soon found that, if heated to 700° C at the same rate as clay brick (270° C in 20 minutes, 520° C in 40 minutes, and 670° C in 60 minutes), the specimens invariably spalled; and that spalling apparently ceased when the rate of heating below 500° C was decreased to 50° C in 15 minutes. Measurements of the linear expansion of bricks during the load tests indicate that the spalling is practically all due to the alpha-beta cristobalite inversion—which takes place at from 220–275° C.² In Table 7 is given the data of such a test. From this data it is seen that there is a decided expansion at the lower temperatures. This is followed by a gradual but very slight expansion until a temperature of approximately 1400° C is reached—at which point a rather decided increase in the rate of expansion is noted. This expansion, which becomes apparent at 1400°, is approximately equivalent to the permanent expansion of the brick. Or, in other words, this ex-

¹ *Loc. cit.*

² The temperature depends upon the previous heat treatment which the material has received.

TABLE 7.—EXPANSION OF BRICK NO. 27 UNDER A LOAD OF 25 POUNDS PER SQUARE INCH.

Time in hours.	Temperature ° C.	Per cent linear expansion.
0.00	19	0.0
1.00	200	0.0
2.50	500	0.340
3.00	650	0.363
4.50	1200	0.403
4.75	1250	0.408
5.00	1300	0.431
5.25	1330	0.431
5.50	1360	0.657
6.00	1400	0.657
6.50	1400	0.657
7.00	1400	0.703
7.50	1400	0.840
Measured cold after test.....		0.158
Total expansion.....		0.840 Per cent
Permanent expansion.....		0.153 Per cent
Difference compared to 0.657 at 1360° C.....		0.682 Per cent

pansion may be considered as due to the actual transformation of silica from the high to low specific-gravity forms.

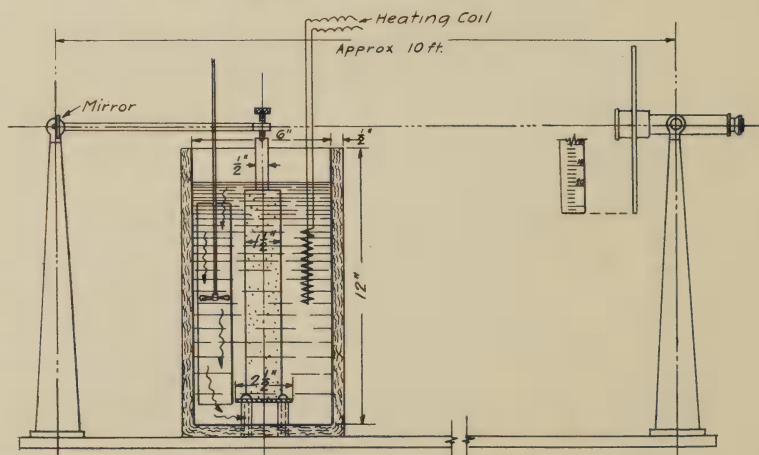


FIG. 6.—Extensometer, designed to measure the expansion of silica brick between atmospheric temperatures and 300° C.

In Fig. 6 is shown an apparatus for measuring the expansion of silica brick up to 300°C . It consists of a lever arm to register expansion and an attached mirror for magnifying the readings to any desired extent by means of a telescope and graduated scale. The test specimen is immersed in a bath of "Crisco," which is heated electrically by means of a nichrome grid. The temperature throughout the bath is kept uniform by stirring the liquid with a paddle. The supports between the specimen and bed plate are of quartz glass, as is also the rod between the specimen and the lever arm. It would be of interest to determine the exact temperatures at which the chief expansions take place for bricks made from each of the leading varieties of quartzite, and also the time required for a standard 9-inch brick to reach its maximum expansion when the temperature is kept constant.

Load Test.

The load test on silica brick is conducted in the usual form of load test furnace.¹ The load is 25 pounds per square inch. The heating rate is 50°C in 15 minutes from atmospheric temperature to 500°C , 75°C in 15 minutes from 500°C to 800°C , 100°C in 15 minutes from 800°C to 1200°C , 50°C in 15 minutes from 1200°C to 1350°C and 30°C in 15 minutes from 1350°C to 1500°C . A temperature of 1500°C is maintained for $1\frac{1}{2}$ hours—after which the firing is discontinued. When cold, the brick should not have increased in length more than two per cent ($\frac{1}{4}$ " per foot), nor decreased in length more than one per cent ($\frac{1}{8}$ " per foot). The Refractory Materials Committee of the American Gas Institute has set one per cent permanent expansion as the limit in such tests. This one per cent limit is a desirable one if materials which will satisfy it can be regularly obtained.

General Results.

Among the more highly metamorphosed quartzites, those which crush largely by breaking through the original grains are apt to yield brick of lower porosity than those in which the breaking is largely through the interstitial material between the built-up

¹ U. S. Bur. Standards, *Tech. Paper* 7.

grains—or those in which a large proportion of the original grains break free from the interstitial material—while the more friable materials, which crush almost entirely to individual grains, show a very high porosity and yield brick which are weak and friable.

Innovations in the methods of manufacture may be advisable in special cases in order to obtain greater uniformity of product. One such innovation is to control the grind so that the percentages of the various-sized particles in the mix will remain constant at all times and to then machine mold the brick at a pressure of approximately 1500 pounds per square inch in order to obtain brick of smooth finish and uniform size.

The porosity of a finished silica brick depends primarily upon the porosity of the unburned mix. However, in so far as the burning does affect their porosity, the lowest porosity will probably be obtained by not allowing the temperature of the kiln to rise above 1350°C until a large percentage of the quartz has had time to be converted to the lower specific-gravity forms. Rapid heating of a silica brick to temperatures above 1350°C , while a large proportion of the silica is still present as quartz, invariably produces a friable (punky) brick. To obtain a brick of comparatively low specific gravity, however, the temperature should eventually be slowly raised to a maximum corresponding to cones 18–20.

The strength of a brick of slight or medium burn (gauged by present practice) is probably due to the glassy bond formed by the interaction of the basic fluxes with the silica, while in well burned brick it appears that the strength is greatly augmented by the formation of interlocking crystals of the low specific-gravity forms of silica. As a general rule, it has been found that silica brick, made from quartzite giving entire satisfaction in other ways, usually meet the strength requirements of service.

Inspection of Ware Based on the Above Observations.

Some of the properties of a finished brick which may be used in judging its probable value in use are as follows: Chemical composition, specific gravity, porosity, cold cross-breaking strength, behavior in the load test, the hot crushing strength

(at the temperature at which bricks are to be used), and the amount of interlocking crystals—determined by viewing thin sections of the brick under the microscope—and the softening temperature of the brick. For the best quality brick these properties, based on available data, approximate the following:

The silica content should not be much under 94 per cent. Bricks containing lower percentages of silica are less refractory. The alkalis should not exceed 0.5 per cent. Greater percentages reduce the refractoriness in direct proportion to their amount. The limit of iron oxide was previously assumed to be 0.5 per cent. However, greater percentages, up to 1.6 per cent, do not appear to materially affect the refractoriness of the brick. The limit for lime is usually set at 2.0 per cent, although larger amounts of lime (up to several per cent) do not greatly lower the softening temperatures. However, in commercial practice, more than 2.0 per cent of lime is considered undesirable.

The average specific gravity for brick made from Medina quartzite, as shown in Table 3, is 2.357 and, for brick made from Baraboo quartzite, it is 2.399. Hence, bricks made from similar materials may be considered as having received a medium burn if their specific gravities correspond to these figures.

The practical limits of porosity which first quality silica brick are apt to have are, Medina 22.80 to 31.52 per cent, and Baraboo 23.45 to 25.66 per cent. However, porosities lower than these might be desirable.

The cold cross-breaking tests, as shown in Table 4 and from other data, should not show an average modulus of rupture much below 500 pounds per square inch. The reliability of this figure is considerably impaired by the comparatively small amount of data upon which it is based.

After having been tested under a load of 25 pounds per square inch at 1500° C, a brick should have neither expanded (linearly) more than two per cent (preferably 1.0 per cent), nor contracted more than one per cent. If desired, the load test furnace may be arranged so that the specimen can be crushed hot at the completion of the test. It would seem desirable to conduct this test at the temperature at which the bricks are to be used.

A micro-examination of a thin section of a brick will detect the amounts of interlocking crystals of the low specific-gravity forms which are present, and thus indicate the degree of burning which the brick received in manufacture.

First quality brick should not have a fusion temperature much below that of cone 31.¹ Cones of the most refractory silica brick bend over at cone 32¹/₂.

Summary.

In summing up, we may say that the bulk of all silica bricks are made from the quartzites of early geologic age, and that, as a rule, the quartzites most suitable for the manufacture of silica brick are those which range from the slightly porous to the highly metamorphosed impervious rocks—having tightly interlocking grains. These may be distinguished in thin section under the microscope, by the fact that the interstitial impurities (such as hydrated iron oxide) appear as sharply defined lines between the tightly interlocking quartz grains, while in material which has been but slightly metamorphosed the interstitial material appears in translucent, cloudy areas between the harder quartz grains. Those quartzites which crush largely by a breaking through of the original grains are apt to yield silica brick of lower porosity than those in which the breaking is largely through the interstitial material between the built up grains, or those in which the original grains break free from the interstitial material.

In special cases, to obtain greater uniformity of product, it may be advisable to control the grind by unusual manipulation—so that the percentages of various-sized particles in the mix will remain constant at all times—and to then mold the brick by machine.

The porosity of a finished silica brick depends primarily upon the porosity of the unburned mix. However, the heating of brick, which contain large percentages of unchanged quartz, to temperatures above 1350° C causes undue expansion—resulting in a punky product. On the other hand, maintaining the tempera-

¹ When ground to pass through a 60-mesh screen and made into cones similar to the standard cones used for comparison.

ture of the kiln at from 1250°C to 1350°C , until a large percentage of the quartz in the bricks has been transformed to the low specific-gravity forms, and then slowly proceeding to the higher temperatures, should result in a low porosity brick of low specific gravity.

The specific gravity of a silica brick, as determined by the wet, dry and suspended weight method, answers as a quick means of determining the degree to which the quartz originally present has been transformed to the lower specific-gravity forms of silica. But to obtain a comprehensive idea of the qualities of any variety of silica bricks, the other properties, such as porosity, cold cross-breaking strength, softening temperature, behavior in the load test, and appearance in thin section under the microscope should also be determined.

COMMUNICATED DISCUSSIONS.

R. M. HOWE: Mr. Ross mentions a great many interesting points arising in the field of silica brick manufacture and gives considerable valuable information.

An interesting point is in connection with his screen analyses as applied to "sand rock." A typical sand-rock analysis follows:

	Per cent.
Retained on 14-mesh sieve.....	0.73
" " 20 " "	2.02
" " 40 " "	42.55
" " 60 " "	46.30
" " 80 " "	7.12
" " 100 " "	0.92
" " 150 " "	0.39
" " 230 " "	0.21
Through 230-mesh sieve.....	0.20
Total.....	100.44

He also mentions the rapidly growing importance of the "specific-gravity" test. Its value is recognized at the present time to such an extent that one company finishes all kilns by means of it. The draw trials are taken from the kilns at intervals and when they have a specific gravity of 2.40 the firing is stopped.

As the kiln is held the brick undergo further transformation—the specific gravities of the brick when drawn being below 2.38. Records are carefully kept, and the firing of each particular kiln may be controlled by this means after sufficient data has been collected.

Mr. Ross, however, makes some statements regarding chemical analysis which are evidently not justified by the work completed to the present time. There is no evidence on record which proves that certain impurities cannot be tolerated. Some materials are high in one particular impurity, but are correspondingly low in other impurities. In view of this and of the necessary incriminating evidence, one cannot justly say as to what percentage of each individual impurity may or may not be tolerated.

As a rule, however, the total percentages of impurities in good grades of silica brick are similar. These generally run between 4.0 and 6.5 per cent. If, then, the total of silica averages in the vicinity of 94.0 per cent or more, about all has been done which can be done. A silica content of 94.0 per cent excludes any superabundance of impurity and yet does not unjustly discriminate against any particular combination of the same. It appears that suitable material can be secured on a silica basis alone. In so doing, the usual exceptions encountered when specifying ceramic materials on the analytical basis will be avoided.

The tests recommended by Mr. Ross have the same general aim. They all tend to develop a well-made, well-burned brick. It is surprising to note how well these same features can be determined instantly by one familiar with a particular brand of silica brick. Two bricks when tapped together show by their ring nearly as much as can be learned by tests. This may be explained by the fact that the raw material is practically the same—the lime bond being kept within narrow limits and most silica brick being sufficiently refractory. The “ring” test determines the variable qualities—the burn and structure. The specific-gravity test, however, goes beyond the scope of the “ring” test in that it is accurate in discriminating between different brands. Some raw materials burn to form a product of good “ring” at low

temperatures. Such materials are quickly detected because of their high specific gravities. This is found to be particularly true when checked by the re-heating (expansion) test.

D. W. Ross: With reference to Mr. Howe's remarks on the above paper, it is of interest to note that in his screen analysis, in determining the size of grain in sandrock (presumably either Homewood sandstone or Oriskany sandstone) large percentages were retained on the 40- and 60-mesh sieves. This apparently checks the results of our own screen analyses.

It is gratifying to know that in so short a time the specific-gravity test for silica brick has been applied in so many useful ways, not the least of which is the method for control of the burning as set forth by Mr. Howe.

Mr. Howe strongly emphasizes the point brought out in the paper, that silica brick, as manufactured in the United States, usually fail on account of their physical properties and not on account of their chemical composition. In our opinion, entirely too much importance has, in the past, been placed on the chemical composition. With this in mind, no presentation of data and detailed discussion has been given in reference to chemical composition. Instead, the merest statement of the results obtained by ourselves and others, and of the usual practice as we understand it, have been set forth. This has been done in order to place on record information which we hope may be of assistance to future investigators in this complex and interesting field—the effects of fluxes, etc., on the properties of silica brick.

ANTIMONY OXIDE AS AN OPACIFIER IN CAST IRON ENAMELS.

By J. B. SHAW, Alfred, N. Y.

Introduction.

The use of antimony oxide in the replacement of tin oxide as an opacifying agent in cast iron enamels has been the subject of a number of investigations. The subject has always been an important one, but there has never been a time when it was so vital as at the present. The present market price of tin oxide makes its use in enamels almost prohibitive. Eight per cent is about the minimum amount of tin oxide that will give satisfactory results in cast iron enamels. At 72 cents per pound, this means that the tin oxide alone in 100 lbs. of raw enamel will cost \$5.76. This was the cost of 100 lbs. of enamel used by the writer in 1913.

Antimony compounds (Leukonin) may be purchased for 16 cents per lb. and antimony oxide is relatively cheap. When it is considered that antimony oxide is equal to tin oxide, pound for pound, as an opacifying agent, it is readily seen that the manufacturers of cast iron enamel wares have a possibility of reducing the cost of their enamels about 100 per cent by the use of antimony oxide.

Staley¹ has presented a very clear statement of the difficulties and possibilities of the problem together with the results of the experiments he has performed. It is not the intention to enter into a detailed discussion of the problem or to repeat what can be readily obtained from the above-mentioned article. Much of the data given herein confirms Staley's conclusions—although on some points our opinions are contradictory. This article will have served its purpose if it stimulates some manufacturer to experiments which result in the successful use of antimony compounds in his enamels.

Antimony oxide has been used successfully as an opacifier in

¹ *Trans. Am. Ceram. Soc.*, 18, 173 (1915).

steel enamels for many years. There is no material difficulty attending its use in the frit for steel enamels, the color being a minor consideration as compared with cast iron enamels—the other constituents of the steel enamel being such as to give better color than those of the cast iron enamels. It may be said that there are no great difficulties attending the use of antimony oxide in cast iron enamels, aside from the obtaining of satisfactory colors. The color, however, is of the first importance—so great in fact that even now, after years of experimenting and when the desirability for its use is so great, antimony oxide is used only in very limited amounts. However, its use is bound to be extended with an increase in the knowledge of how to modify formulas so as to secure satisfactory results.

The results described were obtained in an effort to outline satisfactory working formulas—having antimony oxide as the chief opacifying agent—for commercial use. All have reference to cast iron enamels.

Experimental.

The work was carried out in three stages as follows:

(1) Preliminary batches, hundreds of which were made, were melted in 500-gram quantities in a laboratory furnace. Denver fire clay crucibles were found quite satisfactory for this purpose. It was generally necessary to insert the cold crucible with its batch into the furnace at a temperature of from 1100° to 1300° C. During all of the experiments it was very seldom that the fire-clay crucibles failed under the treatment.

(2) After making laboratory trials with the enamels, those which gave promise of satisfactory results were melted in batches of about 75 lbs. The melted batches were ground and applied on commercial wares. The preliminary melts gave a good indication as to the results which were likely to be obtained with full-sized batches—a great amount of time, money and material being thereby saved.

(3) The enamels were finally melted in batches of about 2000 pounds and applied to commercial ware.

The materials used in compounding the enamels were all of a good commercial grade, the formulas given being figured to a basis of chemically pure materials (feldspar included). A Connecticut feldspar having the following analysis was used:

Chemical analysis.	Per cent.	Formula		
K ₂ O.....	7.30	$\left. \begin{array}{l} 0.62 \text{ K}_2\text{O} \\ 0.38 \text{ Na}_2\text{O} \end{array} \right\} 1.4 \text{ Al}_2\text{O}_3 \left\{ 9.4 \text{ SiO}_2 \right.$		
Na ₂ O.....	2.90			
Al ₂ O ₃	18.60			
SiO ₂	70.40			
Fe ₂ O ₃	0.14			
CaO.....	0.65			
MgO.....	trace			
Loss.....	0.26			
<hr/>		Formula weight, 790.0.		
100.25				

Series 1.

Knowing the efficiency of cryolite as a flux and opacifier in enamels, a number of trials were made with a view to determining the possibility of using it in conjunction with antimony oxide. To this end the following series of enamels was prepared:

SERIES 1.—BATCH WEIGHTS.

No.	Feldspar.	Flint.	Borax.	Soda ash.	Niter.	Fluor-spar.	Cryolite.	Barium carbonate.	Zinc oxide.	Antimony oxide.	PbO.
1	53	0	58	21	26	8	42	0.0	0.0	2.5	0.0
2	73	0	58	28	26	8	29	0.0	0.0	2.5	0.0
3	84	0	58	32	26	8	21	0.0	0.0	2.5	0.0
4	56	24	58	21	25	8	42	0.0	0.0	2.5	0.0
5	73	24	58	28	26	8	29	0.0	0.0	2.5	0.0
6	84	24	58	32	26	8	21	0.0	0.0	2.5	0.0
7	56	54	58	21	26	8	42	0.0	0.0	2.5	0.0
8	73	54	58	28	26	8	29	0.0	0.0	2.5	0.0
9	84	54	58	32	26	8	21	0.0	0.0	2.5	0.0
10	56	0	58	11	26	16	42	0.0	0.0	2.5	0.0
11	73	0	58	17	26	16	29	0.0	0.0	2.5	0.0
12	84	0	58	21	26	16	21	0.0	0.0	2.5	0.0
13	56	24	58	11	26	16	42	0.0	0.0	2.5	0.0
14	73	24	58	17	26	16	29	0.0	0.0	2.5	0.0
15	84	24	58	21	26	16	21	0.0	0.0	2.5	0.0
16	56	54	58	11	26	16	42	0.0	0.0	2.5	0.0
17	73	54	58	17	26	16	29	0.0	0.0	2.5	0.0

SERIES I.—BATCH WEIGHTS—(Continued).

No.	Feld-spar.	Flint.	Borax.	Soda ash.	Niter.	Fluor-spar.	Cryolite.	Barium carbonate.	Zinc oxide.	Antimony oxide.	PbO.
18	84	54	58	21	26	16	21	0.0	0.0	2.5	0.0
19	56	0	58	0	26	23	42	0.0	0.0	2.5	0.0
20	73	0	58	6	26	23	29	0.0	0.0	2.5	0.0
21	84	0	58	11	26	23	21	0.0	0.0	2.5	0.0
22	56	24	58	0	26	23	42	0.0	0.0	2.5	0.0
23	73	24	58	6	26	23	29	0.0	0.0	2.5	0.0
24	84	24	58	11	26	23	21	0.0	0.0	2.5	0.0
25	56	54	58	0	26	23	42	0.0	0.0	2.5	0.0
26	73	54	58	6	26	23	29	0.0	0.0	2.5	0.0
27	84	54	58	11	26	23	21	0.0	0.0	2.5	0.0
28	110	0	58	0	24	23	29	0.0	0.0	3.0	0.0
29	73	25	76	5	19	23	29	0.0	0.0	3.0	0.0
30	73	43	95	0	19	23	29	0.0	0.0	3.0	0.0
31	73	43	58	11	19	16	29	20.0	0.0	3.0	0.0
32	73	43	58	11	19	16	29	0.0	8.0	3.0	0.0
33	73	43	58	0	19	16	29	20.0	8.0	3.0	0.0
34	73	43	67	8	2	12	29	20.0	12.0	5.0	0.0
35	73	43	76	6	2	12	29	20.0	12.0	5.0	0.0
36	73	43	86	3	2	12	29	20.0	12.0	5.0	0.0
37	73	43	95	0	2	12	29	20.0	12.0	5.0	0.0
41	56	66	57	0	7	8	29	20.0	16.0	5.0	22.0
42	56	66	57	0	7	8	29	20.0	20.0	5.0	11.0
43	56	66	57	0	7	8	29	0.0	28.0	5.0	11.0
44	90	0	57	15	17	8	0	0.0	24.0	8.0	11.0

SERIES I.—FORMULAS.

No.	KNaO.	CaO.	BaO.	ZnO.	Al ₂ O ₃ .	SiO ₂ .	B ₂ O ₃ .	PbO.
1	0.9	0.10	0.0	0.0	0.20	0.60	0.30	0.0
2	0.9	0.10	0.0	0.0	0.20	0.60	0.30	0.0
3	0.9	0.10	0.0	0.0	0.20	0.60	0.30	0.0
4	0.9	0.10	0.0	0.0	0.20	1.00	0.30	0.0
5	0.9	0.10	0.0	0.0	0.20	1.00	0.30	0.0
6	0.9	0.10	0.0	0.0	0.20	1.00	0.30	0.0
7	0.9	0.10	0.0	0.0	0.20	1.50	0.30	0.0
8	0.9	0.10	0.0	0.0	0.20	1.50	0.30	0.0
9	0.9	0.10	0.0	0.0	0.20	1.50	0.30	0.0
10	0.8	0.20	0.0	0.0	0.20	0.60	0.30	0.0
11	0.8	0.20	0.0	0.0	0.20	0.60	0.30	0.0
12	0.8	0.20	0.0	0.0	0.20	0.60	0.30	0.0
13	0.8	0.20	0.0	0.0	0.20	1.00	0.30	0.0
14	0.8	0.20	0.0	0.0	0.20	1.00	0.30	0.0

SERIES I.—FORMULAS—(*Continued*).

15	0.8	0.20	0.0	0.0	0.20	1.00	0.30	0.0
16	0.8	0.20	0.0	0.0	0.20	1.50	0.30	0.0
17	0.8	0.20	0.0	0.0	0.20	1.50	0.30	0.0
18	0.8	0.20	0.0	0.0	0.20	1.50	0.30	0.0
19	0.7	0.30	0.0	0.0	0.20	0.60	0.30	0.0
20	0.7	0.30	0.0	0.0	0.20	0.60	0.30	0.0
21	0.7	0.30	0.0	0.0	0.20	0.60	0.30	0.0
22	0.7	0.30	0.0	0.0	0.20	1.00	0.30	0.0
23	0.7	0.30	0.0	0.0	0.20	1.00	0.30	0.0
24	0.7	0.30	0.0	0.0	0.20	1.00	0.30	0.0
25	0.7	0.30	0.0	0.0	0.20	1.50	0.30	0.0
26	0.7	0.30	0.0	0.0	0.20	1.50	0.30	0.0
27	0.7	0.30	0.0	0.0	0.20	1.50	0.30	0.0
28	0.7	0.30	0.0	0.0	0.20	1.20	0.30	0.0
29	0.7	0.30	0.0	0.0	0.27	1.20	0.40	0.0
30	0.7	0.30	0.0	0.0	0.20	1.50	0.50	0.0
31	0.7	0.20	0.1	0.0	0.20	1.50	0.30	0.0
32	0.7	0.20	0.0	0.10	0.20	1.50	0.30	0.0
33	0.6	0.20	0.1	0.10	0.20	1.50	0.30	0.0
34	0.6	0.15	0.1	0.15	0.20	1.50	0.35	0.0
35	0.6	0.15	0.1	0.15	0.20	1.50	0.40	0.0
36	0.6	0.15	0.1	0.15	0.20	1.50	0.45	0.0
37	0.6	0.15	0.1	0.15	0.20	1.50	0.50	0.0
41	0.1	0.40	0.1	0.20	0.17	1.70	0.30	0.10
42	0.1	0.40	0.1	0.25	0.17	1.70	0.30	0.05
43	0.1	0.40	0.0	0.35	0.17	1.70	0.30	0.05
44	0.1	0.39	0.0	0.30	0.16	0.96	0.30	0.05

Results—Series I.

Enamels Nos. 1 to 27 were first tested on small trials. All of these are very fusible with the exception of Nos. 25, 26 and 27. The most brilliant enamels were those highest in silica and lowest in cryolite. Very dull (matt) enamels resulted from high cryolite and low silica contents. The color was fairly good throughout the series but those having the highest gloss—highest silica—generally had the best white color.

The solubility of all of the enamels was determined by partly immersing in water and subjecting them to 15 pounds' steam pressure for 2 hours in an autoclave. The results were as follows:

- Nos. 1 to 6—Very badly decomposed.
Nos. 7 to 8—Much less than preceding.
Nos. 7 to 9—Hardly noticeably affected.
Nos. 10 to 12—Badly etched.
Nos. 13 to 15—Very slightly affected.
No. 16—Distinctly etched.
Nos. 17 to 27—Unaffected.

The above results may be interpreted as follows:

- A. To increase the fusibility: (1) increase alkalies, (2) increase cryolite, (3) decrease silica.
- B. To increase lustre: (1) decrease cryolite, (2) increase silica.
- C. To increase opacity: increase the content of cryolite and antimony.
- D. To decrease solubility: (1) increase fluorspar,¹ (2) decrease cryolite, (3) increase silica.
- E. To purify color: (1) decrease cryolite, (2) increase silica.

After studying the enamels of the series up to No. 27, 75-pound batches of Nos. 23 and 28 were made and applied on commercial ware. The color and opacity were good but both crazed very badly—showing the influence of cryolite in producing crazing. The silica content of these enamels is much higher than that of good commercial enamels not containing cryolite.

Enamels Nos. 29 to 33, inclusive, represent the attempts made to cure the crazing in No. 28. These are all fine white enamels having a high luster. When tested for solubility, No. 32 showed no mark and No. 33 was only slightly dulled in a 2-hour autoclave test.

Nos. 29, 30 and 31 are somewhat decomposed but decidedly superior to Nos. 23 and 28. Nos. 32 and 33 were both too hard and lift or craze in the curves when applied on commercial ware. Nos. 34 to 37 were made in an attempt to cure crazing by an increase of the boric acid content. The crazing gradually decreased up to No. 36, which fitted the iron but was decidedly lacking in covering power.

It was therefore decided that in order to retain the cheapness and stability of the enamel, crazing must be corrected by increasing the silica content. This was attempted, as is represented by enamels Nos. 41 to 43, which crazed and were decidedly harder (more infusible) than the ordinary cast iron enamels. In

¹ This holds true only when smelting is very complete.

order to get a sufficient thickness of enamel to give a good white coat, three or more dredgings were necessary. This required a departure from the usual factory practice and the results were not sufficiently promising to justify their adoption.

Series 2.

The results obtained with the cryolite enamels led to the conclusion that, while good colors were easily obtained, it would not be possible to utilize the fluxing power of cryolite to advantage and that the range of composition within which they would fit the iron would be small. In other words, the factor of safety in cryolite enamels is low. Because of this fact it was deemed advisable to dispense with the use of cryolite and develop satisfactory formulas without it.

To this end the following series was prepared:

SERIES 2.—BATCH WEIGHTS.

No.	Feldspar.	Borax.	Soda ash.	Niter.	Barium carbonate.	Zinc oxide.	Antimony oxide.	Litharge.
47	78	57	49	17	0	8	20	11
48	78	57	39	17	0	16	20	11
49	78	57	29	17	0	20	20	11
50	78	57	49	17	20	0	20	11
51	78	57	39	17	40	0	20	11
52	78	57	29	17	60	0	20	11
53	78	57	49	17	10	4	20	11
54	78	57	39	17	20	8	20	11
55	78	57	29	17	30	12	20	11
56	78	57	22	17	30	16	20	11
57	78	57	17	17	30	20	20	11

FORMULAS.

No.	K ₂ O.	Na ₂ O.	BaO.	ZnO.	Al ₂ O ₃ .	SiO ₂ .	B ₂ O ₃ .	Sb ₂ O ₃ .	PbO.
47	0.14	0.71	0.0	0.10	0.14	0.84	0.3	0.07	0.05
48	0.14	0.61	0.0	0.20	0.14	0.84	0.3	0.07	0.05
49	0.14	0.51	0.0	0.30	0.14	0.84	0.3	0.07	0.05
50	0.14	0.71	0.10	0.0	0.14	0.84	0.3	0.07	0.05
51	0.14	0.61	0.20	0.0	0.14	0.84	0.3	0.07	0.05
52	0.14	0.51	0.30	0.0	0.14	0.84	0.3	0.07	0.05
53	0.14	0.71	0.05	0.05	0.14	0.84	0.3	0.07	0.05
54	0.14	0.61	0.10	0.10	0.14	0.84	0.3	0.07	0.05
55	0.14	0.51	0.15	0.15	0.14	0.84	0.3	0.07	0.05
56	0.14	0.46	0.15	0.20	0.14	0.84	0.3	0.07	0.05
57	0.14	0.41	0.15	0.25	0.14	0.84	0.3	0.07	0.05

Results—Series 2.

This series (Nos. 47 to 57) was a total failure. It is given here in order to bring out the one point of interest which it revealed. All preceding and subsequent enamels in this investigation were first melted in small crucible batches. These 10 enamels were prepared as usual and placed in the furnace, but not one of them could be melted down to a homogeneous solid enamel. All frothed and boiled vigorously and retained the consistency of soap suds after intense heat treatment. A repetition of the series gave the same results. A satisfactory explanation of this phenomenon has not been found. It will be noted that the enamels contained no lime and it was found that a very slight addition of either fluorspar or whiting would cause the enamels to fuse down normally. It has been noted in many cases, since this observation was made, that enamels containing no lime or cryolite are likely to be frothy and smelt with great difficulty and are also likely to repeat this boiling when burned on the ware.

Observations made on this point in many instances substantiate the statement that no very satisfactory enamel can be made in the absence of lime (fluorspar or calcium carbonate), lead or cryolite.

Series 3.

The enamels of the following series represent the type of enamel which has been found by the writer to give the best results when antimony oxide is used as the opacifier:

SERIES 3.—BATCH WEIGHTS.

No.	Feldspar.	Borax.	Soda ash.	Niter.	Fluorspar.	Lith-arge.	Barium carbonate.	Zinc oxide.	Antimony oxide.
58	78	57	39	17	8	11	0	8	17
59	78	57	29	17	8	11	0	16	17
60	78	57	19	17	8	11	20	16	17
61	78	57	6	17	8	11	40	16	17
62	90	57	15	17	8	11	0	24	17
63	95	57	15	17	8	11	0	24	17
64	100	57	13	17	8	11	0	24	17
65	84	57	17	17	8	0	10	24	17
66	90	57	15	17	8	0	10	24	17

No.	FORMULAS.								
	K ₂ O.	Na ₂ O.	CaO.	BaO.	ZnO.	PbO.	Al ₂ O ₃ .	SiO ₂ .	B ₂ O ₃ .
58	0.14	0.61	0.10	0.0	0.10	0.05	0.14	0.84	0.3
59	0.14	0.51	0.10	0.0	0.20	0.05	0.14	0.84	0.3
60	0.14	0.41	0.10	0.10	0.20	0.05	0.14	0.84	0.3
61	0.14	0.31	0.10	0.20	0.20	0.05	0.14	0.84	0.3
62	0.16	0.39	0.10	0.0	0.30	0.05	0.16	0.96	0.3
63	0.17	0.38	0.10	0.0	0.30	0.05	0.17	1.02	0.3
64	0.18	0.37	0.10	0.05	0.30	0.05	0.18	1.08	0.3
65	0.15	0.40	0.10	0.05	0.30	0.0	0.15	0.90	0.3
66	0.16	0.39	0.10	0.10	0.30	0.0	0.16	0.96	0.3

The control of crazing and shivering is best accomplished by varying the silica content. The fusibility of these enamels is quite similar to that of the ordinary tin enamels and the opacity is quite as good as that of enamels in which an equal amount of tin oxide is used.

The color depends largely on the purity and color of the antimony oxide used. Unless the very purest white oxide is used, the color of the enamels is liable to be similar to that of the oxide itself.

Excessive smelting will produce a bluish green color in any antimony enamel containing fluorspar and a low percentage of lead.

A high lead content is not permissible with antimony because the combination produces a yellow color. Blue-white can be converted to pinkish or yellow-white by the careful addition of Venetian Red or Prince's Metallic Brown (ferric oxide) up to 0.4 per cent of the weight of the raw batch.

Thoroughly oxidizing conditions (plenty of niter) must be maintained at all times during the smelting of antimony enamels. Reduction causes the development of a green color. Manganese dioxide (up to 0.4 per cent) may be used to mask the blue-green color of the fluorspar-antimony compound. An ivory-green color results from the use of low fluorspar or insufficient smelting or both. The addition of 1.0 per cent of lead oxide will sometimes convert a useless leadless antimony enamel to one having a pleasing cream color.

Conclusion.

In order to produce antimony enamels of satisfactory color the following should be emphasized:

1. Use only the purest, white, antimony oxide.
2. Use a little fluorspar (not over 5 per cent of the raw batch).
3. Be sure to maintain oxidizing conditions during smelting (use plenty of niter).
4. Control the color by the addition of ferric oxide, manganese dioxide and lead oxide.
5. Cryolite is unsatisfactory as a flux or opacifier in antimony enamels but small quantities (up to 3 per cent) will aid in producing a good color and without introducing any troublesome element.
6. Extreme care in proportioning the raw materials, very careful and thorough mixing, and proper smelting, will insure the successful use of antimony oxide.

ALFRED UNIVERSITY,
ALFRED, N. Y.

DISCUSSION.

E. P. POSTE: Mr. Shaw's paper brings to mind the work of Staley on the control of crazing in cast iron enamels, in which he mentioned the theoretical consideration of the coefficient of expansion. I wonder if Mr. Shaw, or anyone else, has had experience in a case such as he mentioned, *i. e.*, of merely increasing the silica content in order to slightly modify the entire formula so that the theoretical coefficient of expansion will remain the same and in such a way as to retain the same fusibility and at the same time retain the same theoretical coefficient of expansion.

MR. STALEY: I did not understand the remark that was made with reference to my paper.

MR. SHAW: I made the statement that cryolite is not detrimental to the color of antimony enamels; that fluorine, introduced as cryolite, does not produce an unsatisfactory color, and that this is in contradiction to the opinions expressed by Mr. Staley and published in a preceding volume of the Transactions.

MR. STALEY: There seems to be some misunderstanding of my statement. I stated that the objectionable blue color of some antimony oxide enamels is due to a combination of fluorine, boric oxide, calcium and antimony, and that if the calcium and

antimony are in certain proportions and the percentage of fluorine increased—whether by the addition of fluorspar or cryolite—an objectionable blue color will result. I have used large quantities of cryolite in oxide of antimony enamels—in fact to my knowledge practically all of the recipes which are being used commercially for making oxide of antimony enamels contain cryolite.

As near as I can remember, in the empirical formulas of the oxide of antimony enamels, which I know have been used in factory practice, the total amount of sodium and potassium ordinarily found in American enamels falls, in nearly every case, between 0.4 and 0.5 equivalent. The silica content of antimony oxide enamels in this country varies from about 0.75 up to possibly 1.1 equivalents. Mr. Shaw has developed a type of enamel higher in alkalies than those commonly used in this country.

MR. SHAW: I would like to ask Mr. Staley: how would he secure opacity from cryolite in an enamel containing 0.3 equivalent of KNaO ? if he had enough cryolite to secure any fluxing action, how would he keep the KNaO down to 0.3 equivalent?

MR. STALEY: When the total is as low as 0.3 equivalent, the alkali practically all comes from the feldspar and the fluorine is introduced as fluorspar, but if the total alkalies run up to 0.4 equivalent, practically 0.1 equivalent may come from cryolite. The cryolite in percentage weight will run around about 5 per cent of the melted weight of the enamel. Large percentages are not commonly used.

MR. SHAW: I recommend in the formulas that some cryolite, 1 to 3 per cent, be used. You will not secure opacity with 5 per cent of cryolite. If you use less than 8 to 10 per cent of the raw weight, you do not get much fluxing or opacifying value. Referring to the last slide on the screen. Here is shown the type of formula which I not only have been using but am using today on cast iron enamels. I am not stating that anyone here can take any one of these formulas and make a cast iron enamel; that is, at the first trial. There are a number here who can work out a satisfactory enamel from any one of the formulas shown, but

they will have to correct for color, as I stated in the paper. The color is the troublesome part. Here are shown formulas of enamels containing from 0.45 equivalent KNaO up to 0.75 equivalent KNaO . I can take any formula shown and make a satisfactory cast iron enamel. There is no cryolite in any of them, but 3 per cent of cryolite may be added without any detriment to the enamel. I am unable to see the benefits to be derived from the use of cryolite.

AMERICAN CERAMIC SOCIETY.

Acquisition of New Members during October, 1918.

Associate.

- H. M. Thompson, Hazel Atlas Glass Co., Washington, Pa.
M. R. Scott, Bausch & Lomb Optical Co., Rochester, N. Y.
James Gillinder, 111 Orange St., Port Jervis, N. Y.
Miss Dorothy P. Chapman, 31 Shattuck St., Worcester, Mass.
Sanjiro Yamada, Asahi Glass Co., Tokio, Japan.
A. L. Koch, Box 426, Barracks No. 1, Cleveland, Ohio.
Joseph Boughey, 584 Roosevelt Ave., Trenton, N. J.
Miss Anna K. Silver, 9 Hawthorne St., Worcester, Mass.
Edwin L. Hettinger, 1325 Mineral Spring Rd., Reading, Pa.
B. B. Goldsmith, 19 E. 74th St., New York City.
J. F. Sheehy, Alhambra Tile Co., Newport, Ky.

Contributing.

- Vitro Manufacturing Co., Pittsburgh, Pa.
Ohio Pottery Co., Zanesville, Ohio.

JOURNAL

OF THE

AMERICAN CERAMIC SOCIETY

A monthly journal devoted to the arts and sciences related to the silicate industries.

Vol. 1

August, 1918

No. 8

EDITORIALS.

THE ANNUAL MEETING.

The decision of the Board of Trustees to hold the next annual meeting in Pittsburgh on February 3rd, 4th and 5th appears to be a logical one from every viewpoint. Pittsburgh is centrally located, not only as regards railroad facilities, but particularly as regards the distribution of the members of the American Ceramic Society. The meeting should, therefore, be unusually well attended as have those which have been held in Pittsburgh or vicinity in the past.

It is to be hoped that the appeal of the Program Committee for papers to be presented at this meeting will meet with a gratifying response from the membership of the Society. It is to be particularly hoped that our newer members will come to the front and do their share in making this meeting a banner one.

Although our membership has largely increased during the past two years, it will not be an easy task to produce the quantity of high-class contributions necessary for the program of this meeting. When we consider that most of our Government and University laboratories have devoted a large part of their attention to the solution of the numerous War problems which have arisen, and that many of our investigators have been in the Service, we are convinced that unusual efforts will be necessary to bring out the papers for this meeting. The readjustments necessary in many of the Ceramic industries have not been conducive to careful and exhaustive researches of a peace time nature.

It behooves every member of the Society to exert himself in soliciting and producing contributions for the program of this meeting.

TO OUR MEMBERS.

For Americans, November eleventh, 1918, was a far more eventful day and a day fraught with far more radical change in the order of everything than was April 6, 1917.

War, preparation for war and prosecution of war demanded much of all of us, and particularly did it demand a quick adjustment or sudden abandonment of manufacturing, all for a definitely known purpose, and to a definitely known result.

We are now faced by Reconstruction: What of labor, money, prices, etc.? Will freight rates limit or prohibit sources of supplies and markets for manufactured goods?

We do know that our boys are coming back, most of them immediately—our transportation facilities will be required less and less for troops and munitions. We now have better equipped rail facilities and a growing merchant marine, all of which spells Prosperity. None can see and only a few—a very few—dare predict when, or how the prosperity will come. Rumors of prosperity and of depression are deductions from the same data and conditions, and by equally well posted minds.

These things are sure; Americans, individually and collectively, have more money, are more optimistic, have more resources, and have learned the value of preparedness so—Now that the Governmental restrictions and guidance, and committee interference are no more, each individual and concern must again gird for competition. The clarion call for Ceramic workers is to Organize—Organize—for all purposes but in no other as much as for strength technically.

As sure as the seas are now wide open and traversed by hundreds of more freighters, so surely will competition be more keen. War found us unprepared—behind the times. We caught up—but was it not most largely because of pooled interests and federal guidance? Will Reconstruction find us unprepared?

The American Ceramic Society has gone a long way on the necessary road to preparedness by the several changes in rules,

establishment of Local Sections, publication of a Journal, but it must go much farther. We must organize the Professional Divisions at once and make a drive for new members. We must have more contributions to our literature—both practical and technical. We must have more coöperation with other scientific societies.

Now all boost—get together—bring in your neighbors that we, united in one for effective team work, may the better and the quicker prepare for the technical demands of a world-wide competition. The Society is yours and the officers are your servants—write to them your ideas—contribute to the JOURNAL—and be sure to remember that your Society—your Organized Technical Preparedness Effort—needs the Contributing Membership of your firm and Associate Membership of your fellow-worker.

BOOST! for Prosperity is here.

ROSS C. PURDY,

Chairman of Membership Committee.

DIRECTORY OF DEALERS.

Attention is called to the advertisement on another page of the "Directory of Dealers in Raw Ceramic Materials," published by the American Ceramic Society.

This pamphlet was compiled by the Sub-Committee on Clays and Raw Materials for the Clay Industry, and contains the names of 671 firms dealing in kaolins, ball clays, flint, feldspar, plastic and flint fire-clays, limes, etc. These are listed in two ways; first, the firms are placed alphabetically, with the chief materials carried by each; second, the materials are arranged alphabetically and the firms from whom they may be obtained are, listed under each. There is a supplementary list of special glaze and body materials, with the names of the dealers carrying them.

The bulletin is comprehensive and will be valuable to those who buy the various raw materials of the ceramic industry.

ORIGINAL PAPERS AND DISCUSSIONS.

NEWCOMB POTTERY.

I. HISTORY OF NEWCOMB POTTERY.

BY MARY G. SHEERER.

The Newcomb Pottery was started through a desire of the Art Department of Newcomb College to provide a means of bringing the work of its graduate students before the public. There was little or no opportunity in the South at that time (1894-5), for these students except to teach, so the Department undertook to make a way for them.

The governing motive of the Newcomb Art School has been to bring art into every phase of life; not to confine it to the teaching of picture making, or statuary, but to connect it as well with household furnishings, such as pottery, china, textile decorations, book-binding, jewelry, etc.

In 1885 an art league was formed in New Orleans under the supervision of Wm. Wordwerd, professor of art at Tulane University. The league conducted a pottery for five years and many very creditable pieces came from its kilns, but, owing to lack of capital, it was unable to continue. Like so many other efforts which seem to fail, however, it proved to be the suggestion for the more substantially planned pottery which followed it some five years later at Newcomb.

Active experiments were begun in October, 1895. In one end of a large room was built a round kiln with four fire boxes. There were in the same room a kick-wheel, drying shelves, tubs for clay, tables, decorator's working outfits, exhibition shelves and tables, glaze pots and a hand-mill for grinding. No tenement room was ever used for so many purposes, but there



FIG. 1.—First home of Newcomb Pottery.



FIG. 2.—Present home of Newcomb Pottery.

was interest, enthusiasm, and activity aplenty—and great expectations!

The services of a potter from the Golf Juan Pottery at Cannes, France, were secured and to him was entrusted the making of forms on the wheel, glazing and firing.

The writer came from the Cincinnati Art School to conduct classes in the decoration of pottery and its appreciation. The president of the College, and the director of the Art School with the well-equipped students from the Newcomb Art School, completed the personnel of the pottery force.

A cream colored clay and a red clay, locally procured, were washed by hand in tubs. Clear glazes, from French recipes, were ground in a hand-mill and experiments were made on both both clays by slip painting, biscuit painting, inlaying and modeling. From a sample collection of underglaze colors, two blues, a green and a yellow were selected. Considerable work was done with slip painting, entire back-grounds being put on by spraying with a cup atomizer.

Design was such a strong feature at the Art School that the



FIG. 3.—Corner of present salesroom.

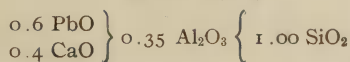
decoration was mainly simple and good from the beginning, but slip painting was found difficult to control in this warm climate where the windows and draughts are many, so it was soon abolished in favor of biscuit painting.

The character of the decoration came about through a natural growth. After abandoning slip painting the designs were drawn and painted on the biscuit. After unsuccessful attempts to secure the desired texture on the clay surface as it came from the wheel, it was decided to produce the texture with the sponge on the green or unfired piece. This led to designing on the wet clay and incising the designs and painting after the first fire. This gave more variety and depth to the effect and the method still continues in use.

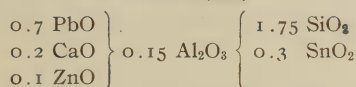
The last few years have seen a marked growth of interest in the hand-built pottery. The personal touch and variety of surface which these pieces afford give added charm to the glaze and no decoration of the form is needed.

A matt glaze which is used on this ware has a wide range and is good in texture. Following is its formula and also that of a tin glaze used:

MATT GLAZE



TIN GLAZE



II. TECHNICAL PRACTICE AT THE NEWCOMB POTTERY.

By PAUL E. COX.

Introduction.

In view of the fact that the Newcomb Pottery will be moved to new quarters sometime during this year, it seems fitting that this termination of what might be called the "second period of the life of Newcomb Pottery" be marked by a report of the technical development to the present time.

The writer believes that Newcomb Pottery has been bettered and that the reputation of the pottery as an art product has been enhanced by the application of the principles taught in the ceramic schools, and that an art pottery is great only when it recognizes

that technical merit is a close second to good design in decoration, or good taste in choice of coloring, and that a leaky, badly glazed and fired vase, no matter how perfect the design or how lovely the coloring, is bad and unworthy of a place of merit. This refers, of course, only to contemporary pottery, since there is no excuse for anything to the contrary being made in the light of our present knowledge.

Body Mixtures.—The body in use at Newcomb Pottery eight years ago was reported as made of a mixture of Biloxi clays Nos. 1 and 2, Iuka clay, Texas kaolin, and feldspar. The Biloxi clays were secured from a bluff close to Biloxi, Miss., and were reached by a schooner working its way up the bayou on which the clay was found. These clays had been used locally by flower-pot and charcoal makers and were also rather excellent for the purposes of pottery making, but were not easily accessible—since there was little method in handling the overburden of the deposit and a large amount of waste material was necessarily removed each time clay was taken out. As a consequence, when opportunity offered a clay that was more easily obtained, a change was made.

The body made from the above clay mixture was covered with a clear glaze and fired at between cones 02 and 1. The ware was porous, crazed badly, and had little to recommend it except that the body was easily worked on the wheel and in the class rooms.

Since Newcomb Pottery is indigenous to Louisiana in decoration and spirit, it was desirable that the clay be obtained in Louisiana. Samples of clay from Covington, a point across the river in St. Tammany Parish, close to the city of New Orleans, proved workable and the body as now used is composed as follows: 35 per cent Covington clay, 45 per cent Paducah ball-clay, and 20 per cent feldspar. The Paducah ball-clay was chosen only because it gave satisfaction and was easily obtained. It might be replaced by other light-burning clays.

The above body burns dense at between cones 3 and 5 (the cones used), and works well on the wheel—though a little contrary for large pieces—does not leak when fired even a little soft,

and the glazes stand well without crazing. The decoration being put on by cutting away part of the clay, the mixture must be well lawned and free from grit in order to secure good results. Since a thorough sponging of the surface is made by the designer for the sake of the proper texture for the later painting, there must be little washing away of the clay in the process. The above body was developed with these objects in view and has proven successful.

According to the writer's observations of the tests of different clays on the wheel by the very skillful throwers working at Newcomb Pottery, coupled with tests by himself on the wheel, he is inclined to question whether or not a satisfactory definition of plasticity has ever been made. The clay in use at Newcomb Pottery would usually be rated as a very plastic one, and yet large pieces are made from it with difficulty because the pieces settle after the first draft is made. On the other hand, small pieces are made with the utmost facility. Other clays used, one from Fish River, Alabama, for example, are not open to the same criticism, but are worthless for pottery making. Still others are entirely satisfactory in all respects. Tall pieces are made on the wheel more easily from sandy clays than from fat clays. Many very fat clays which have been tested on the wheel could not be thrown at all, but were otherwise of the sort that would be considered plastic. No tests other than wheel tests were ever made.

Preparation of Body.—Owing to the fact that the sand from the very sandy local clays worked back from the end of the shaker lawn and into the lawned slip cistern, and that the lawns wore out so rapidly and at such inopportune times, shaker frames were discarded. A trough was arranged to separate most of the sand by means of a series of baffles and the slip was then poured through the lawn—a single one of 150 mesh. It has been found that better clay and more of it for a given period can be had by this arrangement than with a machine. The Covington clay consists of about one-third white sand, which wears the metal lawns rapidly, so that this seemingly more primitive method is the better one.

From the cistern, the slip is pumped into a 100 gallon tank to which air at 100 pounds pressure is admitted. This tank is connected to the filter press and the air under pressure forces out the water. The writer has found that a compressed air system for pressing clay does away with the nuisance of the overflow valve, presses a more uniform cake of clay without soft centers, is easier on the sacks, and that a press of clay may be made at night while the rest of the machinery is not working.

We have found that there is no need for agitation of the slip in the tank if there is as much clay to keep the inert matter in suspension as there is in this body. Any industry using natural clays can save very largely in installation cost and subsequent repairs by the substitution of a tight tank for the slip cistern and by running the slip by gravity to the tank. No difficulties from sedimentation will be met with—if reasonable care is taken to clear the tank once a week or oftener—and better clay cakes will come from the press. The writer has had a chance to test out many kinds of filter-press sacks and has found that the twilled press sack material, used in most sugar houses, is better than the canvas used in most clay plants. It does not become clogged so quickly and is more easily washed out and does better work in every way.

Molding and Decorating the Ware.—All ware made at Newcomb Pottery is thrown and turned—the same wheel being used for turning as for the throwing.

In a leather-hard condition, the ware goes to the designer, who sketches the design and scrapes and cuts away a part of the clay so that the design is in slight relief. After drying at room temperature, the ware is biscuited to cone 012, and is then painted by the artist who designed it—the colors being underglazes supplied by color dealers. The glaze coating is then put on and the ware fired a second time at between cones 4 and 5.

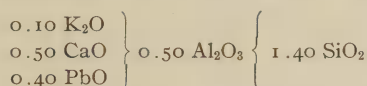
Glazing.—The inside glaze coating is applied by the use of a pump—since the ware must never be touched on the outside by the fingers. Even the dry clay pieces must not be touched in placing in the biscuit kiln as any finger marks will show. The surface obtained by the sponging process is so delicate that finger

marks are filled in by the wash of blue with which the values are obtained and show in a very unsightly way after the glost fire.

The outside coating of glaze is applied by dipping, the pieces being handled by the bare bottoms and the uncolored rims. The bottoms are then sponged free of glaze, the untouched rim is covered with glaze by means of the air brush, and two coats are added all over with the same air brush.

Several coatings of glaze are applied. By the use of colored dyes, confusion in the glazing is avoided. After applying the first coating a colored (dye) glaze coating is applied to a table full of ware. This is followed by a coating of another color and this provides a standard glaze coat which is free from crawling and gives to the colors put on the values desired by the decorators. Nearly all of the losses are due to too thick glaze coating and even with the system outlined, mistakes in judgment occur.

The glaze now in use has the following formula:



The dry glaze mixture is ground in the ball-mill with denatured alcohol and then applied with the spray. This glaze does not flow when applied but dries at once and can be handled rather freely. At times, it is desirable to put a coating of colored glaze over a piece that is not so desirable from the standpoint of color and this easy method has saved many a dollar that would have otherwise been lost. By the use of a glaze maturing at a lower temperature, and by grinding in alcohol as indicated, the cooler parts of the kiln are utilized with considerable gain.

In a general way the writer has decided that, whatever the theory under which matt glazes are developed may be, the nature of the body on which they are to be used must be reckoned with and, if a glaze with a wide firing range together with freedom from crazing is desired, the clay content must be high and silica content low. In a general way, our experience at Newcomb Pottery agrees with that of others as to the types of formulas giving the best matt glazes.

It will be noted that the clay content in the above matt glaze

is very high. For a time we used calcined clay and gum of tragacanth in the glaze. The gum proving troublesome, it was eliminated to the advantage of the product. The calcination of the clay was next discontinued and the glaze was found to adhere to the ware better. Difficulties from crawling were overcome by the use of the air brush and a thin first dipping. It is the writer's opinion that there is no reason for the crawling of art pottery glazes, no matter what formula is used, provided the glaze work is given careful attention.

Kilns.—The two kilns are round, down draft, one being 6 feet and the other 5 feet diameter, outside, the larger one taking six and the smaller three bungs of saggers. Each kiln has two fire boxes. An iron case, $\frac{3}{16}$ " thick, encloses the brick work of each and, in order to make wicket building easy, a flat arch tops the doors. The doors are built up of special sagger clay blocks made at the pottery. The flat arches were made by supporting the outside ends of the bricks by a plate of iron, so that only the ends of the bricks are exposed to the high temperatures—the bricks being driven in place tightly and with no mortar.

The smaller kiln is used for biscuit—since the biscuit can be doubled in placing. About four-fifths of the glost kiln produces satisfactory, well-burned ware and the space left is used in a way which will be described later.

Distillate is used for fuel. This is stored in a thousand gallon tank in the pottery yard, the oil being forced to the kiln burners by pressure from a small volume blower which injects the oil into the fire box in a stream from the central tube of the burner. The surrounding tube of the burner furnishes air in a volume sufficient to break the oil into a spray and to furnish much of the air for combustion. The volume blower forces air into the oil storage tank and the air-tube of the burner is connected to a pipe that takes its supply from the storage tank so that the oil tank serves as an air reservoir as well. Pressure of about eight pounds is maintained by the blower. The oil gives little trouble—aside from the deposit of masses of carbon which sometimes divert the path of the flame so that the ware suffers from reduction and blistering. This does not often happen and the losses in the kiln

last year were under three per cent—mostly caused by other reasons than kiln accidents. To burn the two kilns, with an average of 120 pieces in each, requires 150 gallons of distillate costing from $6\frac{1}{2}$ to $7\frac{1}{2}$ cents per gallon delivered.

Saggers.—For sagger-grog, waste fire brick are crushed in a laboratory crusher. The mixture of raw sagger clay is prepared by washing in a blunger. It is washed as thick as it can be handled in the machine and then poured into a galvanized iron pan resting over a furnace. A coarse screen takes out the bits of clam shell and oyster shell, that cause “poppers” if not removed, and the dry grog is then added. The sagger mixture is as follows:

30 per cent by volume	New Orleans Clay
30 per cent by volume	Biloxi No. 1 Clay
40 per cent by volume	grog

The mixture is ground as stiff as possible in a wet-pan and then wedged by hand.

The New Orleans clay is that deposited by the river and its sand content varies. In the clay state, the saggings stand a great deal of rough handling without damage, due to this gummy New Orleans clay which, when fired, vitrifies so that the saggings are both open and strong. The clay does not burn dense by itself because of its content of sand. Saggings made of the above mixture have been in use from ten to twenty times a year for five years and, in some cases, six years, and are still in excellent condition. The writer feels that this is a better sagger body than is usually met with in this sort of work and under the conditions laid down.

Placing.—The ware is burned in a low biscuit and a high glost fire so that most of the shrinkage takes place in the second fire. Consequently, it is not safe to place the glost pieces on stilts. The glaze is removed from the bottoms of the pieces and—except in the case of pieces with wide bottoms which are not liable to topple over—the pieces are placed on the bottoms of the saggings. Since this is done, the saggings are not glazed inside, as we have found that in a 14-hour burn there is no advantage in so doing, and, furthermore, the glazed saggings have a shorter life. The

bottom of each sagger is coated with a wash of refractory clay and, since the bottoms of the pieces have been cleaned of glaze, little of this adheres to the pieces. This method has almost entirely prevented kiln losses through sticking. It is desirable to have the bottom of a pot glazed, but not desirable enough to risk the loss of a piece after so much work has been done upon it.

One of our sources of loss has been the blistering of pieces exposed to a slight reducing flame and, since the fire boxes are a large part of these small kilns, the saggars are subject to more reduction than they would be in a larger kiln. In case the glaze coating is too thin, the addition of another thin coating will make the piece a choice one. In fact, the best ware is often that which has had a third firing with a thin added coat of glaze. However, there is comparatively little of this sort of work to be done, so that if the piece is valuable the expense is justified.

The work reported in this paper would have been done by any man trained for the job and there is nothing startling to report. However, some others, with the same problems to solve, may find helpful hints. No claim for perfection in methods is made by the writer—this paper merely tells what has been done. Most of the methods followed were make-shift ones, but the Pottery speaks for itself.

NEWCOMB POTTERY,
NEW ORLEANS, LA.

A CONVEYOR STOVE ROOM.

By C. E. JACKSON, Wheeling, W. Va.

Much progress has been made in the pottery industry within the last few years and especially in kiln construction. However, very little attention has been paid to one of the most vital departments of a pottery, *viz.*, the clay shop in which all of the ware is formed. We do not believe it possible to change its fundamental or basic operations. We assume that it will always be necessary to use molds made of plaster of paris or of some other material that will give the same result. Therefore, any advancement that can be made in this department will have to be in the simplification of its well-known operations. It was with this object in view that the writer undertook to eliminate some of the trouble that attends the manufacture of goods, generally known as flat-wares, and which are made on the machines called jiggers.

It has been the custom to consider the operating jigger unit as consisting of a jigger-man, a batter-out, one or two mold runners, and a stationary stove room. The function of this stove room is to receive the molds on which the ware is formed in the wet state and to give sufficient capacity to retain the same until dry. This means that the size of the stationary stove room is largely governed by the number of molds necessary for the day's operations. Let us assume that this number averages from 175 to 200 dozen per jigger-man—and that the number of stoves in the jiggering department is in proportion to the number of jigger-men.

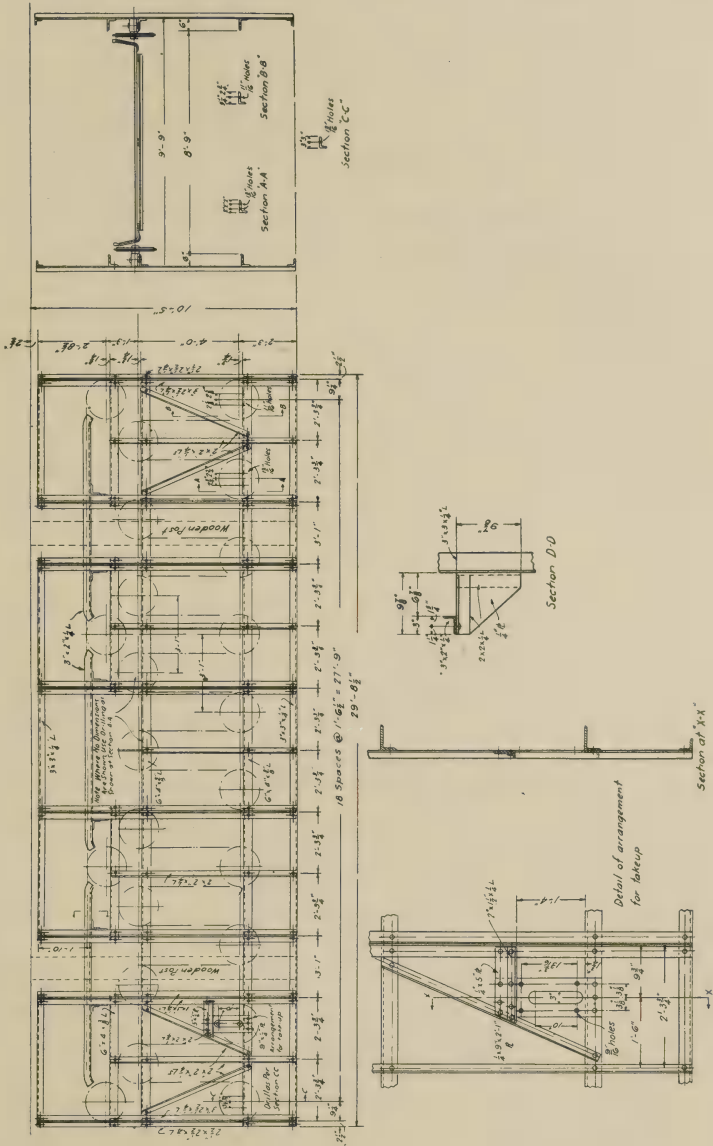
Since the operating unit consists of a jigger-man and two (or in some cases three) male helpers, we will consider an operating unit as consisting of a jigger-man and his attendant labor. The attendant labor has always been the obstacle in the steady production of the jiggering department. It has usually consisted of boys and young men, in most cases irresponsible. When this attendant labor fails to come to work, it means that the output for that operating unit is lost for the day, and this becomes a

constant occurrence. Furthermore, the efforts of the jigger-man, instead of being devoted to the making of the pieces of ware at hand, are largely given to the control of his attendant labor. Owing to the passage of the Child Labor Law in the various states, it became very difficult to obtain this attendant labor, and even more so after we entered the War. Various plans have been suggested and talked over for the elimination of this attendant labor. In Europe, the problem had been partly solved by the use of a bat-making machine, but there still remained the question of getting the molds to and from the stove room which necessitated attendant help for the jigger-man. We endeavored, therefore, to take advantage of the partially worked out system in vogue in Europe, and, by the use of a conveyor operating in conjunction with a bat-making machine, to totally eliminate all attendant labor. The writer is pleased to state that this has been accomplished in a most satisfactory manner.

A conveyor system, consisting of two lengths of chain operating on parallel lines on sprockets, and carrying shelves on which are placed the molds, was designed and constructed. After filling, the molds are placed by the jigger-man on the shelves of the conveyor. A movement of the chain carries the shelves to the rear of the conveyor where they are emptied by the finisher. The empty molds are then returned to the jigger-man for refilling.

In an installation of this kind there are many things to be considered. There is no question that the system requires more space than the old stationary stove room, but in a different manner. The old stationary stove room required considerable space running the length of the shop while the conveyor requires depth or height. By referring to the drawing it will be noted that the chain travels up and down nine times. We found this travel necessary in order to secure the length of chain required. Had the ceiling been higher, we would have made the conveyor higher and the up and down movements fewer.

Very few potteries present greater obstacles than ours in the establishment of this system. However, it is necessary to understand the fundamental principles of conveying machinery before



installing the system. The first decision to be made is the number of molds the conveyor is to carry. If the number of dozens of ware per machine per day is decided upon, and the molds are to be filled but once a day, then sufficient chain length to allow the required number of shelves is necessary. However, we must bear in mind that the production per day, using the conveyor type of stove room, will be less than by the use of the old system—owing to the fact that the jigger-man has no attendant labor whatever. We have found the difference to be about 25 per cent. While this is true per day, the number of dozen pieces of ware produced during a period of 30 days will be greater—owing to the fact that a jigger-man will work full time. Using the old stove room, with attendant labor, the efficiency was not more than from 60 to 75 per cent. It is necessary, therefore, to take this into consideration in figuring an installation.

Sufficient heating apparatus is necessary for the drying of the molds and ware in transit. We have found the use of exhaust steam pipes laid on the floor under the conveyor to be the most advantageous. In considering the installation of the steam pipe system, it is necessary to take into account the fact that, on the overhead return of the conveyor, the molds have been emptied by the finisher, which means that only 75 per cent of the molds in the conveyor are actually drying the ware.

The batting-out machine is constructed on the same principle as the spreader—which is nothing more nor less than a flattening-out tool working on a revolving plaster whirler. The jigger-man places a piece of clay of the desired size on the whirler (when stationary) and then throws the machine into gear. The action of the down coming arm forming the bat is automatic with the revolving whirler. After the bat has been made, the arm being released, returns to its original position, the whirler being again stationary. This is all being done while the operator is making a piece of ware. The operator, working at right angles to the machine, lifts the mold out of the jigger-head with the left hand and places it on the conveyor shelf which stands at the level of the jigger box. With the same movement he places another empty mold for filling.

The three mechanical movements necessary, *viz.*, that of the

batting-out machine, the operation of the jigger, and the movement of the conveyor, can all be controlled by one mechanical movement as exemplified in the machine for this purpose placed on the market by the Potters Equipment Co., 200 5th Ave., New York, N. Y. In our case, each unit is operated separately.

Although the action is very simple, the advantages to be gained by this system are: First, the elimination of attendant labor; second; continuity of output; third, the jigger-man has nothing to detract his attention from the work at hand. By its use we find that the drying is more uniform, the production is more uniform from all angles, the ware is of better quality, and there is less loss in our biscuit ware room. Comparing the earning power of the jigger-man against the old method, we find that with the new system, the average earning of the jigger-man is higher by about 10 per cent. We are able to keep our shop much cleaner—which is conducive to the health of the employees. While an equipment of this kind is somewhat expensive, we believe that the advantages to be gained are sufficient to justify the installation.

WARWICK CHINA CO.

PREPARATION AND APPLICATION OF ENAMELS FOR CAST IRON.¹

BY HOMER F. STALEY, Washington, D. C.

ENAMEL MAKING DEPARTMENT.

The enamel making department, usually known as the "mill room," comprises facilities for storing, weighing and mixing raw chemicals, furnaces for melting the enamels, enamel dryers, and mills for grinding and sifting the enamel.

1. Storing, Weighing and Mixing the Raw Materials.

Of course the relative arrangement of these various parts can be varied at will. A commonly used and convenient arrangement is a three-story building with the melting furnaces at one side or end. The crude raw materials are stored on the third floor. They are sifted there by mechanical riddles and then fed into chutes leading to bins on the second floor. The sifting not only removes any nails, pieces of twine, etc., that may have gotten into the raw materials, but also serves to break up the lumps that commonly form in powdered chemicals. The absence of lumps greatly facilitates the fusion of the enamel to a homogeneous glass.

On the second floor the weighing and mixing of the batches are carried on. In one arrangement the bins are built in a long row with their bottoms a few feet above the floor level. A set of scales on wheels runs on a track in front of this row of bins. The chemicals can be scraped by a hoe as desired from the various bins. Gravity feed of the powdered chemicals into the weighing box has not proven successful. Part of the time they stick and do not feed at all, and the rest of the time they come down with a rush. This system eliminates all shoveling, but entails considerable moving of the scales and partially completed mix back and forth. In another system, the bins are arranged in a circle around the scales. The chemicals can be scraped into the weighing box by means of a hoe and troughs, but often are simply

¹ By permission of the Director, Bureau of Standards.

shoveled in. Multiple-beam scales, weighing at least six ingredients with a single setting, are commonly used.

The mixing of the raw batch should be very thorough. With small batches this is often done by "cutting" the completed mix with shovels. Care should be taken to see that each shovelful of the mix is actually turned over in each of at least three cuttings. After this the whole mix should be run through as fine a riddle as possible. With large batches, mechanical mixers of various types are employed. In general, it may be said that batch mixers are more satisfactory than continuous ones, and that the drum type, in which the whole mix is thrown over and over, is better than the trough type, in which mixing blades travel through the batch lying in a stationary container. In continuous mixers, the portion fed into the machine first comes out first and therefore the batch as a whole is never blended. When dependence is placed on mixing blades in a stationary trough or a fixed container of other shape, a layer next to the shell is not mixed in with the rest.

A simple and efficient batch mixer of the drum type consists of a ball-mill without any balls. A lining is not necessary. If desired, three or four stout bars may be inserted midway between the circumference and axis and extending from one end of the mill to the other. These are not necessary, neither are shelves to carry the mix up the sides of the mill. If a batch, not filling the mill over two-thirds full, is run in a plain ball-mill, without balls, at a proper speed for five minutes, it will be found to be very thoroughly mixed.

A convenient location for the mixer is below the floor level of the weighing floor but above the level of the top of the melting furnaces. If not more than three furnaces are to be fed from one mixer and these are built close together, the material may be dumped into a stationary hopper and fed into the top of the furnace, by spouts. The angle of the feed spouts with the horizontal should be at least 60 degrees. When the material is to be carried a greater distance, a hopper-bottomed car or lorry running over the tops of the furnaces is convenient. The sides of this hopper should also form an angle of at least 60 degrees with the

horizontal. It is too hot on top of a furnace to permit of dislodging material that sticks in a hopper or spout.

2. Melting the Enamel.

Melting Furnaces.—The furnaces used for melting enamel are of the reverberatory type. They are similar to the ordinary potters frit kiln but larger, some of them holding over two tons of melted enamel. They are simply large boxes with inclined bottoms and low arched roofs. The raw material is fed in batches at the top, or side, and drawn off periodically from a tap-hole on one side. Many efforts have been made to operate melting furnaces continuously but without much success up to the present time. The heat is obtained from a flame passing across the kiln just beneath the roof. Various attempts have been made to build frit kilns that would be heated from below, without contact of the combustion gases with the frit, but no material has been found that will transmit the heat readily and yet resist the intense corroding action of the molten frit. In Fig. 1 are shown the drawings of a frit furnace used in several plants. It will be noticed that the arch of this furnace does not drop down as it approaches the end away from the fire. A dropping arch is more expensive to build than a straight one, and proper approach of the flame to the melt can be obtained by regulation of the height of the arch as a whole, the slope of the floor and the outlet of the chimney. In another type of furnace, the position of the melting chamber is reversed from that shown in these drawings, the flame traveling across the short dimension. In this type the extraction of heat from the flame is not quite as complete as in the case where the flame travels lengthwise of the melting chamber. When the furnace is used for oil or gas, part of the fire box is bricked up and a checker-work of fire brick is placed on top of the brick filling.

In some cases a second melting chamber for melting ground coat glass has been built onto the cold end or side of the enamel melting chamber, the idea being to utilize for melting the ground coat glass some of the heat that ordinarily goes up the chimney. These have not proven very successful, mainly because the heat obtained is not sufficient to do much melting and supplementary

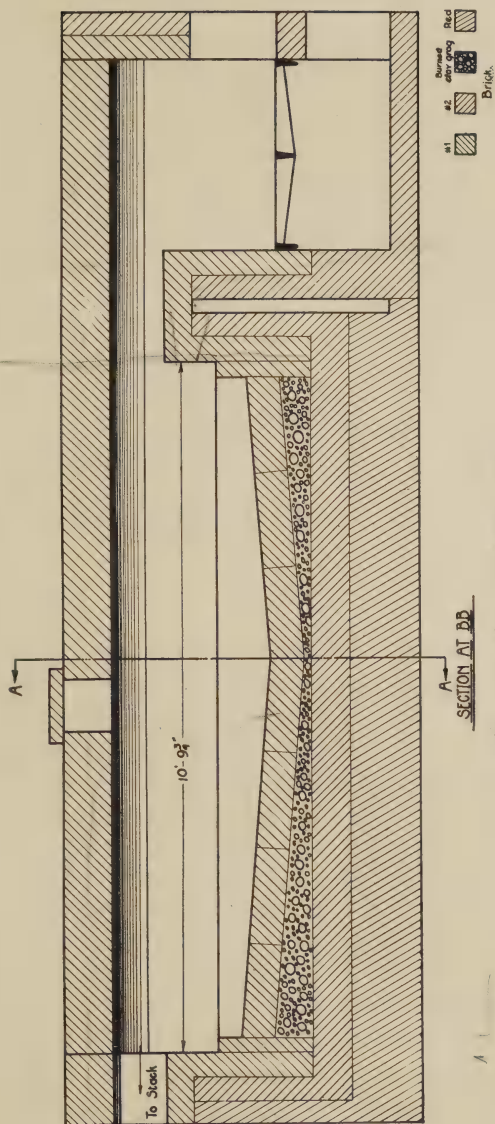


FIG. 1a.—Enamel Melting Furnace.

burners have to be installed. When the bridge-wall between the two melting chambers is not built hollow, the glass from one tank works through into the other. The melting tank for ground coat should be built like that for the cover coat but may be smaller. For ground coat glasses that are to be drawn while viscous, the

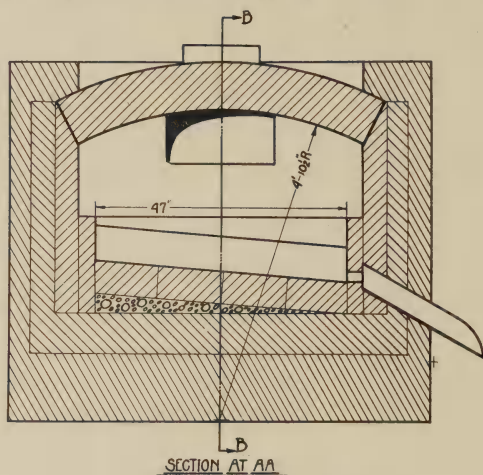


FIG. 1b.

tap-hole may be left about four inches square and stopped up by a couple of wedge brick. Sometimes ground coat glass is melted simply to a very viscous mass in scrap sinks, placed in the hottest part of an enameling furnace for 18 to 24 hours.

For melting enamels, natural gas, producer-gas, or oil should be used for fuel. With coal and coke, too much dust and ash is deposited on the melting enamel. Whatever kind of fuel is used, the flame should be thoroughly oxidizing, that is, a blue flame, free from smoke and incandescent carbon—which make a yellow flame. The least fuel is used when the draft is so regulated that the tip of the flame just reaches across the furnace. A shorter flame means that too much air is being used, and a longer one means that the stack instead of the enamel is being heated.

The Melting Process.—After the raw enamel batch is put into the melting tank, it is pushed back against the walls in every direction from the tap hole. This is done because the deepest

part of the melting tank is at the tap-hole, and if the top of the charge is made level it is difficult to melt the material deep down near the tap-hole. In the course of one to four hours, depending on the size of the batch, the melting is finished. The amount of stirring that should be done during the melting depends on the uniformity of the mixing of the raw batch, the type of furnace, and the kind of enamel. The finer the grains of the materials composing the batch and the more uniformly they are blended, the less the necessity for stirring. If a furnace of large capacity, compared to the size of the batch, is used, so that the material can be spread out in a thin layer, stirring is not so necessary. Using thoroughly blended batches and large capacity furnaces, the author seldom found it necessary to stir tin enamels. In order to get uniform color in antimony enamels, stirring of the mix toward the end of the melting period must nearly always be practiced.

The objection to stirring enamels, aside from the small amount of labor involved, is contamination of the melt with iron from the stirring rods. It has been found that cheap tool steel rods give less scale than rod iron. The enamel adhering to the rods should never be broken off into the tank for holding good enamel. If the rods are chilled in a separate barrel of water, the dirty enamel may be saved and remelted with a new batch. In order to avoid stirring of the enamel, one company, making steel tanks, goes to the length of melting the enamel in what is virtually a large rocking ladle.

Tin enamels are nearly always tapped off within a few minutes after bubbling ceases. It was formerly held that this was necessary in order to prevent the enamel from overheating and becoming contaminated with metallic lead and tin. With better control over and understanding of our fires, we find that this reduction was not due to overheating but to reducing conditions in the flame and combustion gases used for melting. With a good clear blue flame, a tin enamel may be heated for hours after bubbling ceases without changing color. As explained in another section, the tint of antimony enamels varies greatly with the amount of heating they undergo. All enamels depending

in part on fluorides for opacity, especially fluorspar, become less opaque on continued heating.

3. Dryers.

The enamel is tapped out into a large tank into which a supply of cold water, amply sufficient to chill it, is running and is then taken to the dryers. One type of enamel dryer consists of a large revolving iron drum with a fire beneath it. A certain amount of fine iron scale is ground off this drum into each batch of enamel. In other cases the enamel is dried in thick layers in large pans heated by waste gases from a furnace or melting tank or by a separate fire. The enamel must be stirred in these in order to get it dried in a reasonable length of time and to prevent it from sticking to the pans, which become quite hot. In still another method the enamel is spread in thin layers in pans placed on racks in large drying cupboards. These are generally heated by gas. In this method no stirring is necessary and there is little contamination of the enamel, but the amount of room devoted to drying must be large. Rotary dryers, lined with porcelain blocks and having projecting shelves made by inserting rows of deeper porcelain blocks, have been built. These are heated by blowing hot air through them. They must be made quite large compared to their capacity, for if the blast of air traveling through them is strong, it blows out all the fine particles of enamel.

4. Grinding Machinery.

For grinding enamel, ball mills are used almost universally. Porcelain brick are nearly always used for lining. Formerly flint pebbles were used for grinding, but in late years the use of hard-burned porcelain balls has largely superseded them. Any particles ground off the balls show up less in the enamel than similar particles from the dark flint pebbles, and, when a good grade of porcelain is used, the balls wear less than the pebbles. While very hard and resistant to abrasion, the pebbles are brittle, and are often destroyed by splitting. The balls are worn down by abrasion a little more rapidly than the pebbles, but seldom split. Mills of from 250 pounds capacity per charge up to 3000 pounds are used. The size is largely a matter of choice, some of the largest plants using the smallest mills. Often large and small

mills are used in the same plant. Some enamel makers claim that with small mills there is less contamination of the enamel by abrasion of the linings and balls, but this is largely a matter of proper regulation of the charge and speed of the mill. Large mills require less labor for a given capacity.

In a few cases continuous ball mills, or tube mills, have been used. These have not proven very satisfactory, mainly because the output is small compared to the amount of power used and the money invested in the machines. The charge in a tube mill does not more than half fill the machine, while in ball mills, the charge usually fills the machine to 75 per cent of its capacity. Hence, the charge in the ball mills is more nearly balanced on the center of gravity of the machine and at the same time is larger—resulting in a greater output for a given amount of power and volume capacity of mills.

Whatever type or size is used, great care should be taken to see that no metal is exposed to abrasion. This is most likely to occur around the door frames. The resulting contamination of the glass causes black specks, which are especially noticeable in antimony enamels. Care should also be taken to prevent contamination of the enamel by grease and dirt from pulleys, belts and bearings. The wear on linings and balls will be lessened and the contamination from that source greatly reduced, if arrangements are made to empty the ball mills while they are running at a very slow speed.

Cover enamels are ground dry to a fineness such that they will pass a 60-mesh sieve. Ground coat enamels are usually ground wet to extreme fineness.

5. Screens.

In a few plants the enamel is not really screened in the mill room, being simply shoveled through a coarse riddle to take out lumps of enamel and small pieces of mill lining and stones. It has been found that the small amount of coarse material in the enamel powder seriously interferes with the speed of application of the enamel, and all enamel is screened in the mill room at most plants. The screen wire used is commonly about 10 meshes finer than that used in the dredges, *i. e.*, the sieves used in applying the enamel to castings.

Various types of screens are used, revolving screens probably being the most common. In order to get the enamel powder through these they must be jarred. Formerly, this was commonly done by an iron hammer hitting on a ring of iron knobs encircling the center of the screen. With the introduction of antimony enamels, it was found that the contamination of the enamel by specks of metal from these knobs and the hammer was very noticeable. The use of rawhide hammers reduced the dirt somewhat and changed the specks from iron specks to carbon specks, produced by particles of rawhide. Various expedients have been employed to overcome this trouble with revolving screens, the most practicable of which seems to be the placing of the beater ring and hammer at one end of the screen frame, beyond the screening area. This eliminates the dirt but cuts down the capacity of the screen, since the jarring action is greatly reduced.

Another screen is of the reciprocating type. A flat screen is hung from a frame by wire cables and made to move back and forth by a short-stroke air motor such as is used for foundry riddles. Such a screen is clean and well suited to plants of moderate capacity. To keep down dust, it may be enclosed in a cabinet, the motor being placed on the outside. Of course, the air motor may be replaced by a belt-driven eccentric or any other mechanical device that will give a reciprocating motion.

A sifter adapted from the flour milling industry has a combined rotary and sliding movement. An oblong screen is set in a box with a solid bottom. One end of this box runs on rollers, while the other end, which is slightly higher, is supported by a ball and socket joint on the end of a pin set eccentrically on a horizontally running wheel. The sifter is operated by power applied to this wheel by an adjustable friction drive. As the pulley revolves, the upper end of the box takes a rotary motion while the lower end runs back and forth on the rollers. The horizontal pulley, and of course the upper end of the box, make about two hundred and thirty revolutions a minute. The enamel passing through the screen slides down the inclined bottom of the box and out through a chute at the lower end. The coarse material passes out through a similar chute at the lower end of the screen. Since

all wearing surfaces in this machine are below the floor of the box in which the enamel is sifted and caught, there is no contamination of the enamel powder from that source. The capacity of this screen, as well as of the sliding screen previously described, may be materially increased by attaching to the screen frame a compressed air vibrator, such as is used for vibrating molds in foundries.

THE ENAMELING PROCESS.

1. Application of the Ground Coat.

After being sand-blasted and cleaned, the castings should be kept in a dry, warm place until ground-coated, which should be done within a few hours. The ground coat can be applied by painting, pouring, or spraying. In painting, a ground coat composition of about the consistency of thick gravy is spread over the surfaces to be enameled by means of flat painter's brushes—four-inch brushes are used for tubs and two-inch for small ware. The brush marks are likely to show through the enamel, especially if the piece is heated strongly during the firing of the ground coat or enamel. The heat causes incipient blistering and swelling of the heavier ridges left by the brush. For this reason, painting of ground coats is not extensively practiced. Sometimes when certain parts of a piece are to have an especially thick coat, these are painted before the piece is poured or sprayed.

In pouring, enamel of about the consistency of cream is poured over the casting. If the piece is small, it is turned in various positions and rocked backward and forward on two rods extending over a drip tub until the ground coat is smoothly on the surface of the whole piece. The thicker beads, that accumulate at the edges, are removed by running a finger along them. In the case of tubs and other large pieces, the ground coat is poured on as uniformly as possible, then the piece is placed in various positions and pounded with a rawhide mallet. The vibration tends to cause the coat to run smooth. When done by a skilled man, working with ground coat enamel of proper consistency, coatings of very fair uniformity can be produced by pouring. It is a more rapid method than painting but not as rapid as spraying.

It is by spraying that the most uniform coats are applied, and at the same time with the greatest speed. The spraying devices are operated by compressed air, various types being sold for the purpose. In addition, a number of kinds of home-made sprayers are used in different plants. In general, it has been found that sprayers which depend on suction for their supply of coating give finer-grained and more uniform sprays than those depending on pressure. The sprays should be as fine grained as is consistent with reasonable speed of operation. The ware is usually placed on a turn-table while being sprayed. In some shops, small ware is sprayed on a regular small-ware enameling table.

In spraying, only one-third to two-thirds of the material coming from the spray nozzle lights on the ware. Therefore, the spraying space should have a smooth wooden floor and smooth wooden walls on three sides. If the castings are clean all over before they go to the spraying cabinet and the workmen do not carry in dirt on their feet, the ground coat on the floor and adhering to the walls may be gathered up, sieved and used over again. Dust from cement or brick walls and floors is liable to contaminate the ground coat.

If an exhaust fan is used to carry away the vapors from the spray chamber, a large box or collection bin should be placed in the pipe line. This will act like a dust collector and most of the material carried away will be deposited. It is best not to try to use this for ground coat alone but to mix it in small proportions with fresh coat.

The following simple device for conserving labor and material in the spraying of tubs is in use in several plants: The tub is run on a truck into a three-sided wooden stall having a runway around the top of the sides, which extend a few inches above the rim of the tub. The operator walks around the tub on this runway, spraying as he goes. The waste material is caught by the sides of the stall and may be used again.

After being ground-coated, the ware must be kept in a dry warm place until enameled in order to avoid incipient rusting of the iron. This time should be brief, twenty-four hours at the most. Usually the pieces are stored near the enameling furnaces.

2. Enameling Room Equipment.

The enameling room is usually rectangular in shape with furnaces along one side. This room should be well lighted and ventilated and have a high roof, the lowest girders being at least twenty feet from the floor. A high roof not only makes a better ventilated room, but reduces the amount of enamel powder and dust that lights on the girders and drops or is blown down from time to time. Latticed monitors and in fact any kind of ventilators that can retain dust are also objectionable. The overhead girders and underside of the roof should never be white washed, as the coating peels off and spoils any hot enameled surface onto which it drops. When furnaces are built on both sides of the room it is likely to be dark and is always very hot.

The furnaces used for enameling cast iron are large rectangular ovens having an arched roof and a wide door at one end. If coal is used for fuel, the sides and arch are built double, forming a tight muffle. If gas is used, the inner arch is sometimes omitted, thus making a semi-muffle. For tubs, the inside dimensions of the muffles are about nine feet long, six feet wide, and five feet high to the crown of the arch. Small ware furnaces are made about six feet square by four feet high, inside dimensions.

Various types of furnaces are used, most of the variations being made in the flue systems. Very elaborate flue systems have been embodied in furnace construction with the idea that the longer the length of travel of the flue gases in the furnaces the greater the amount of heat given up. This, of course, is not necessarily true. These elongated flues are generally placed in the roof and sides of the furnace, which receive large amounts of heat by radiation and conduction from the muffle and heating flues proper, and it happens often that the combustion gases leave the flues at a temperature fully as high as that at which they entered. In other words, heat cannot be withdrawn from gases by leading them through heated flues. In other cases, these flues are placed farther away from the hot parts of the kiln and nearer the outside surfaces. The gases then leave the flues at temperatures somewhat lower than the entering temperatures. However, the heat given up simply goes to heat portions of the kiln exterior that are normally cool and to increase the radiation from these. The

only way possible to extract heat in useful form from hot flue gases is to use the hot gases for heating the air used for combustion—by means of some form of regenerator or recuperator.

In general, it may be said that the simple types of furnaces give the greatest satisfaction. Complicated flue systems are prone to result in poor draft and frequent stoppage of flues with soot. The more complicated the construction of a kiln, the greater is the possibility of its going to pieces under the strains incident to expansion and contraction of the furnace on heating and cooling. Complicated furnaces are expensive to build, difficult to operate, and expensive to keep in repair.

In Fig. 2 is given the plan for a tub furnace that has been used with good results in several plants. Part of the flame from each burner goes directly up along the wall and over the top to the central collecting flue. The main portion passes under the floor, up the opposite side, and over the top to the same collecting flue. The distribution of the flame is controlled by the dampers. By using a short flame, most of the heat is generated under the bottom and in the lower ends of the side flues and the products of combustion enter the collection flue at a comparatively low temperature. The material for this furnace can be had at reasonable prices since the construction calls for no special shapes, except the cup brick for the muffle, and these are used in large quantities by the enameling and other industries. As shown, the furnace is intended for the use of natural gas, producer-gas, or oil. The burners are placed alternately on the sides of the furnace. When used for coal, fire boxes are added at one side, each fire box serving two flues, and all the firing is done from the one side. By removing the top arch of the muffle, this furnace can be readily converted into an open arch, or, in other words, a semi-muffle furnace.

In a few plants, double-chamber furnaces of this type are used, the firing being all done on one side. One part of the products of combustion passes under the floor of both chambers and up the far wall of the second. The other part passes entirely over the top of the first chamber, through the division wall near the floor level, and up the inner side of the second chamber. The first chamber is always a tight muffle, but the second is usually

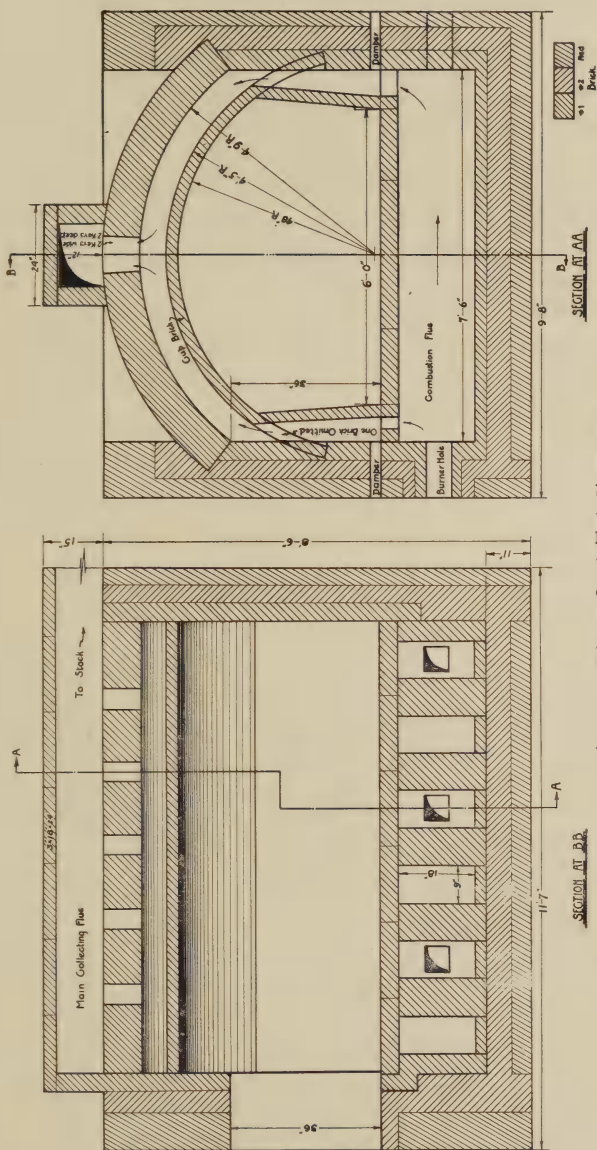


FIG. 2.—Direct-fired Tub Furnace.

operated as a semi-muffle furnace. The final melting of the ground coat and all baking of enamels is conducted in the first chamber, which is kept at ordinary enameling furnace temperatures. The second chamber, which usually is at a dull red heat, is employed for preheating the tubs, covered with ground coat, to dull redness.

From a double furnace, more pieces can be turned out in a given time with less expenditure of fuel per piece than from a single furnace. However, since the double furnaces save nothing in labor, this rapid rate of working is very severe on the workmen and often causes dissatisfaction.

Another type of furnace which has come into use in a few plants burning gas or oil has no fire boxes. Flames are turned directly into the furnace chamber so as to heat it to a temperature suitable for enameling. The supply of fuel is then shut off and the tub is enameled simply by the radiant heat of the hot furnace walls. As soon as the tub is removed from the furnace, the flames are turned on again. This type of furnace is cheaply constructed and very economical in the use of fuel.

In Europe, where fuel is very expensive, a number of types of enameling furnaces equipped with recuperators have been built. A few such furnaces have been constructed in this country, after European designs. In Fig. 3¹ is shown the plans of a European furnace with a recuperator built integral with it. It will be noticed that the large fire box is, when covered with a very thick bed of fuel, really a gas-producer. This feature is one of the chief advantages of such furnaces. The air for combustion of the gases produced travels around the tubes of the recuperator and is preheated by the out-going combustion gases. According to Damour,² recuperation of secondary air for furnaces with a working temperature of 1800° F. will give a fuel economy of 30 per cent. These furnaces give good satisfaction, but it is a question how much of this efficiency is due to the recuperative feature and how much to the gas-producer and heavy, heat-retaining construction in general. The first cost of these furnaces is quite

¹ E. A. Schott, *Stahl u. Eisen*, 30, 1556.

² Emilio Damour, "Industrial Furnaces," p. 127. (Published by *Engineering and Mining Journal*.)

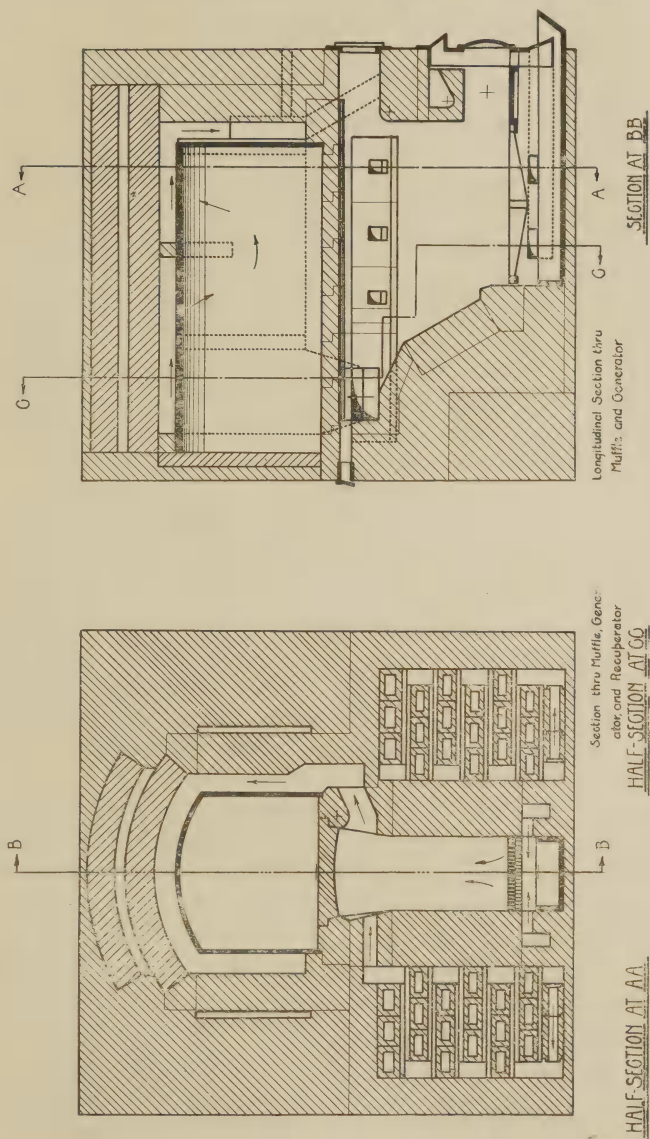


FIG. 3.—Muffle Oven with Recuperator System.

high—usually about double the cost of a simple direct-fired furnace.

The fuel consumption of any of the foregoing furnaces can be materially decreased by covering them with a layer of some of the heat insulating materials now on the market. In regard to irons and braces, it may be said that the more substantial these are the less the cost for repairs to the furnace. In regard to the use of open arches versus tight muffles—it is to be considered that where open arches call for much less fuel than closed arches, their use is more likely to give ware of poor finish and contaminated with dirt from the roof of the furnace.

The doors to the furnace may swing sidewise, rise up, or drop down. Swinging doors, whether single or double, suck out hot air when opened and push in cold air when closed. Lift doors are liable to cause dirt to be dropped onto a piece of ware being taken out of, or put into, the furnace. Dropping doors are the cleanest and do not cause air currents. The only disadvantage is that it is not possible for the enameLER to open them a little way in order to observe a piece of ware in the furnace. Of course, opening a door to look at ware is merely a matter of habit and convenience, for the piece can always be inspected through a peep-hole left in the door. Rising doors are most commonly used. In most plants, compressed air is used for operating tub-furnace doors—a simple hoist with a wire cable running over sheaves being the common apparatus. In some plants electricity is employed. Occasionally, power is used to open small-ware furnace doors, but the more common practice is to have them opened by hand. Power-operated rising and dropping doors are counter poised so that they are self-opening, the power being used simply for closing and keeping them closed. This greatly reduces the mechanical problem of operating the doors and at the same time gives assurance that the furnace will be open for the extraction of ware if anything goes wrong with the power.

Supporting the Ware.—The ware, while being enameled, is placed on a rack or table, known as an enameling table. This table is fitted with gears and levers which permit the top being tilted at any angle to the perpendicular, or even turned upside down in some types, and revolved while in the various positions.

Any good master-mechanic can design such a table and consequently there are many varieties being used, most of them being indigenous to the shops in which they are found. In general, the tables are tilted on the main horizontal axle of the frame and revolved around a pin extending through this axle. In tables not intended to have the top turned completely over, the center of rotation is placed between the two bearings of the main axle. In tables whose tops are to be completely reversed, the center of rotation is placed on an end of the main axle extending beyond both bearings. Similar tables are used for enameling small ware but in most cases these are operated by hand.

Formerly a hand crank was used for rotating enameling table tops, but in the more modern plants the tops are rotated by power. One type of table uses a reciprocating air motor, which produces a rotary movement by means of a series of cams articulating with gears. Such tables are jerky in their action. A much more satisfactory method is the gearing of a rotary air-motor or small electric motor to the mechanism ordinarily used for rotating the table top by hand. The top should rotate at a speed of ten to twenty revolutions per minute. With an air motor the speed can be largely regulated simply by the amount of opening of the foot-valve used. The tilting is still commonly done by hand, but in a few shops this is done by the use of a small air hoist and suitable sheaves and pulleys.

For supporting the ware in the furnaces while being heated, various sorts of racks, called "bucks," are used. These are generally made of heavy sections of cast iron. Sometimes old railroad rails are used for bucks for tubs and, less frequently, blocks of fire clay. The latter do not warp nor deteriorate by oxidation like metal but are difficult to shift about into proper positions in hot furnaces. The best form of buck for tall cylindrical pieces, such as lavatory pedestals and drinking fountains, is a heavy base with an extension curved so that a long finger points horizontally toward the door of the furnace. The pieces are fired on this finger and, being in the horizontal position, are heated much more uniformly than when fired in an upright position.

The ware is put into and taken out of the furnaces by long

two-pronged forks, which are suspended either from a crane or from a trolley running on an I-beam. Sometimes dirt drops off the I-beam into ware, but the trolley system is steadier and easier to handle than the cranes. In a few plants the forks are pivoted on a truck running on tracks extending out from the front of the furnaces. This is a clean system, but does not permit of ready adjustment of the fulcrum point of the fork to ware of different heights.

Application of the Enamel.—Enamel powder is kept more free from dust and is more readily obtained by the operators working at high speed while enameling, if it is kept in a covered receptacle from which it can be made to feed semi-automatically in fixed quantities into the enameling sieves or dredges. Such contrivances are generally known in the shops as "powder dummies." One form of dummy consists of a large funnel with a drum at the bottom divided into six wedge-shaped compartments. The drum rotates on its horizontal axis and, except at the bottom and top, is entirely encased by close fitting walls. Whenever the contrivance is not being operated, one of these compartments forms the lower end of the large funnel. When he needs enamel powder, the operator pushes with his sieve on a rod reaching below the drum, the movement of this rod operating a pawl which causes the drum to rotate one-sixth of its circumference. In this way one of the compartments is emptied into the sieve.

A much more simple form of dummy consists of a large circular funnel with a tubular extension on the bottom. This extension is closed by a swinging slide with a weighted projection at the bottom. To operate this dummy, the enameler pushes with his dredge on the weighted projection. The slide is thus pushed back and the sieve brought into position under the tube, the enamel in the tube immediately dropping into the dredge. When the pressure is removed, the weight on the projection causes the slide to close. The enamel in the funnel proper slowly drops down to fill the tube again. This simple contrivance is much less likely to get out of order and costs less for repairs than any of the more complicated dummies.

For protecting tubs from drafts during cooling, covered stalls, called "dog houses," just large enough to hold one tub on a truck, are provided. The front of these stalls may be open or may be provided with loose fitting doors. Tight doors do not allow a tub to cool fast enough and thus favor the growth of minute crystals on the surface of the ware, which cause dull finish. These stalls may be built of any solid material. Sheet iron is not suitable, especially for the roof. The light sections of metal buckle with heat from a hot tub and throw dirt onto the still soft enamel. It is not customary to use cooling chambers for small ware.

The dredges used for sifting the enamel onto the ware consist of circular sieves attached to handles about five feet long. In order to have the enamel pass through the screen in an even stream, the sieves must be vibrated. In a few shops this is still done by rapping the wooden handle of a dredge with a beater. The beater consists of a small oval hoop of about $\frac{3}{8}$ " round iron having a wooden handle fastened to one end. The oval is placed around the handle of the dredge and worked rapidly up and down by the right hand of the enameler while the dredge is held by his left hand, and, in the case of large sieves, partially supported by a counterpoise. The more common method of vibrating dredges is by means of a small air or electric vibrator attached to the end of a gas-pipe handle on the dredge. The common form of air vibrator is a small chipping hammer with a blunt point substituted for the chisel. This may be a long rod with its tapping end beating against a plate attached to the wall of the sieve, or it may be very short and beat against a hardened disk held in a case at the end of the dredge handle. Since the whole dredge, including the handle, must be vibrated in either case, the point of application of the blows is obviously immaterial. Electrically operated vibrators of several types have been used, but they have not proven as satisfactory as the air hammers. The introduction of mechanical vibrators for enamel dredges has been a great boon to the enameling industry. They enable the workmen to produce more and better ware with much less effort. Formerly, paralysis of the hand used for beating was not uncommon among enamellers. For hand vibrated

dredges, 30 to 40 mesh-wire gauze is used, while for power-vibrated, 40 to 60-mesh is employed.

3. Enameling a Bath Tub.

Having previously been coated with ground coat, which must be perfectly dry, the tub is caught up along the under side of the rim by one of the large forks, operated by the two enamellers, and placed in the furnace. In from seven to ten minutes, the iron is a bright, cherry-red, and the ground coat has melted evenly. The piece is quickly withdrawn and placed on the revolving table. One man sifts enamel on the rim through a small sieve while the other man dredges the sides and bottom. The heat of the iron fuses the enamel enough to make it stick to the surface. In about three minutes the piece is thoroughly covered, and is immediately put back into the furnace. In a few minutes the enamel has melted smooth, and the tub is drawn and given another coat. This runs smooth in a few minutes, and the piece is again drawn. Any blisters appearing are patched by being perforated by a steel point and covered with a little mound of enamel powder. The tub is given a third light coat and allowed to bake. It is then drawn, any enamel that has run over the edge of the casting is trimmed off with a large knife, and the piece is allowed to cool in a "dog house."

The proper enameling of a tub is a matter of considerable skill and judgment. Each dredge must be evenly distributed over the piece. If it is too thin in places, blue spots show on the finished ware; if too thick, crazing or chipping off of the enamel may occur. One fault especially difficult to avoid is the tendency of the enamel to run and collect in rolls or beads at certain points. This spoils the appearance of the piece and often results in crazing when the tub cools.

The temperature at which practically all tub enamels mature is very close to 1000°C (1800°F). It may not be much higher, for between 1050° and 1100°C (1900 and 2000°F), cast iron burns "dead," becoming exceedingly weak and brittle. It cannot be much lower on account of the increased cost. An enamel that would mature much earlier would have to be considerably higher in the more expensive fluxes. Another important con-

sideration is that an enamel which would mature much earlier would be a softer glass, more readily soluble, and more liable to deteriorate under the ordinary conditions of use. An enamel for cast iron that will meet all the requirements of the service for which it is intended can be made at 1800°F .

Though the enamel matures at 1800°F , the furnace is fired to a considerably higher temperature. The temperature is kept down by the process of enameling. Every thirty minutes, or thereabouts, a cold tub weighing from 200 to 300 pounds is put in, heated to 1800° , drawn out three times, allowed to cool considerably and heated up again after each cooling. This process keeps the furnace and the men busy, insuring a maximum output of ware, but it calls for skill and watchfulness on the part of the enameler. Each coat of enamel is baked very quickly; it is melted down in from two to five minutes in a rapidly rising heat. Exposure for a minute too long in the furnace during any one of the four heating periods may ruin the piece. The defect may be burning up of the slush coat, sulphur bubbles, running off of the enamel, etc. If the tub is not heated sufficiently, the result will be pin holes in the coldest parts, and a rough, uneven coat, of poor luster.

After the tub is cold, it is carefully inspected as to defects in application and fit of the enamel, color, luster, etc. Minute crazes are readily detected by rubbing the surface with a rag filled with black grease. The tub is then painted on the outside, supplied with feet and fittings, and taken to the ware room.

A PYCNOMETER OPERATED AS A VOLUMETER.¹

By H. G. SCHURECHT, Columbus, Ohio.

Owing to the fact that in studying the drying and burning behavior of clays, the volume shrinkage can be determined more accurately than the linear shrinkage,² a satisfactory volumeter for measuring this shrinkage is an important piece of apparatus in a ceramic laboratory. Heretofore, the Seger volumeter,³ although unsatisfactory, has been used almost universally. Some of the objections to the Seger volumeter are enumerated as follows:

1. It is too time consuming. In order to obtain accurate results with a Seger volumeter, it is necessary to allow the liquid in the burette to drain at least 3 minutes before making a reading. The total time required for a single determination of volume varies from 5 to 10 minutes.
2. Particles of grit or clay may become lodged in the large stopper joint—thus changing the volume of the bottle when closed.
3. It is quite fragile and easily broken.
4. Errors are often introduced through the entrapping of air bubbles.

Pycnometer Volumeter.—In order to overcome some of these objections a volumeter (Fig. 1) operating on the principle of the pycnometer was used in the Bureau of Mines Laboratories with excellent results. The bottle is made of glass—metal being considered too heavy as it would decrease the sensitiveness of the balance and thereby decrease the accuracy of the determination.

¹ By permission of the Director, U. S. Bureau of Mines.

² J. Bailey, "Variation in Linear Shrinkage of Clay Test Pieces," *Trans. Am. Ceram. Soc.*, **18**, 557-563 (1916).

³ For details regarding operation of the Seger volumeter see H. Ries, "Clays, their Occurrence, Properties and Uses," Robert Drummond & Co., N. Y., pp. 160-62.

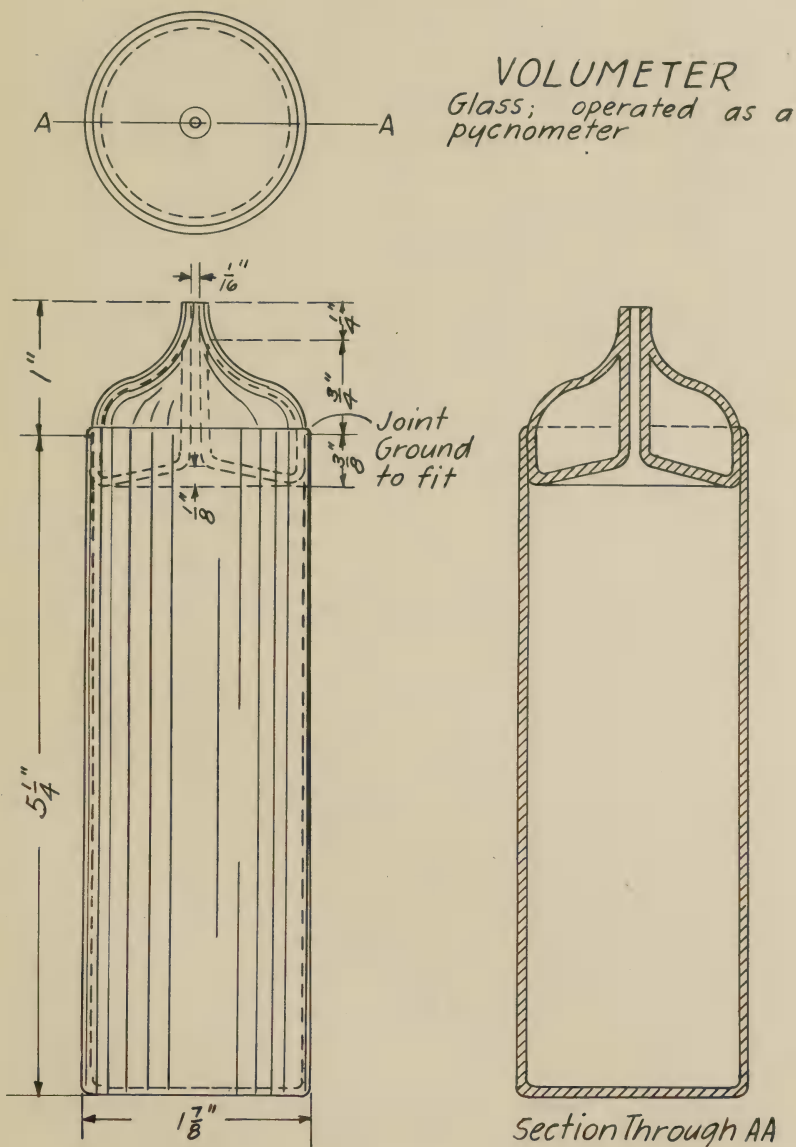


FIG. 1.

Operation.—The bottle is filled with liquid (kerosene or water) and, as the stopper is inserted, sufficient liquid is forced into the tube in the stopper so as to fill it completely. The excess liquid is carefully wiped off and the bottle is weighed. The briquette to be measured is then inserted into the bottle and the operation is repeated. The calculation involved is as follows:

$$V = \frac{W - W_1 + B}{S}$$

V = Volume

W = Weight of bottle plus liquid

W_1 = Weight of bottle plus liquid plus briquette

B = Weight of saturated briquette

S = Specific gravity of liquid

It is necessary to check the weight of the bottle plus the liquid at intervals as minute particles of clay, dropping from the briquettes, may increase this weight.

A mark is scratched on one side of the stopper and bottle so that the stopper may be placed each time in the same position with reference to the bottle—any error which might be caused by inserting the stopper in different positions being thereby eliminated.

In comparing this type of volumeter with the Seger volumeter it might be said:

1. That it is much more rapid, in that a determination can be made in from 1 to 2 minutes as compared with the 5 to 10 minutes required when using the Seger volumeter.
2. It is very accurate. Volumes can be determined to within 0.01 to 0.05 cc.—the accuracy depending on the size of the briquette and the sensitiveness of the balance used.
3. The error due to the lodging of grit or clay in the joint of the stopper and to forcing the stopper further down into the bottle in one case than in another would be less in this apparatus than with the Seger volumeter—as the stopper of the former is smaller and the displacement would be smaller in proportion.
4. There is less chance of error from air bubbles.
5. It is not as easily broken as the Seger volumeter.
6. It is less expensive.

COMMUNICATED DISCUSSION

By F. GELSTHARP,

OF THE PAPER

"THE EFFECT OF CERTAIN IMPURITIES IN CAUSING MILKINESS IN OPTICAL GLASS."

By C. N. FENNER AND J. B. FERGUSON.¹

The Pittsburgh Plate Glass Company has been very successful in producing the several types of optical glass. Although in our early work we occasionally encountered milky or opalescent glass, either in the pot or after molding, we have not observed the phenomenon for a long while. The only glasses in which this opalescence was produced were the borosilicate crown (refractive index 1.522) and dense flint (refractive index 1.616). Impure potassium carbonate was not the cause of the opalescence because the pure nitrate was used in place of carbonate. I do not feel that the authors of this paper have positively proven that the presence of sulphates in certain optical glasses will produce opacity or milkiness.

This is a very interesting subject to glass manufacturers generally as opalescence has been the cause of trouble in other branches of the glass industry. When ordinary soda-lime glasses turn milky or slightly opalescent, the milkiness may invariably be eliminated by a slight increase in the alkali content of the glass.

From the small amount of research work I have done on simple glasses, I believe that I am correct in stating that, having a supersaturated solution of silica, the tendency is for this to precipitate out, either on cooling slowly, or, if the cooling is too rapid, it will separate on reheating. I therefore propose a different view for the solution of this problem.

The optical glass referred to by the authors and those glasses which I have mentioned contain a very high molecular content of silica and therefore approach supersaturated solutions. If for some reason the alkali content is lower than intended, milk-

¹ *J. Am. Ceram. Soc.*, **1**, 468-476 (1918).

iness may easily result. I would offer the following explanations for this:

First: In the case of Russian potash, if a batch were made up containing 68 parts by weight of potash (calculated to anhydrous K_2CO_3 assuming that the KCl and K_2SO_4 present will supply their quota of K_2O) to 300 parts of sand, it is very probable that there would be a deficiency in alkali sufficient to produce a supersaturated solution. In case melts from this batch did not opalesce, probably a higher temperature prevailed and the K_2SO_4 dissociated or reacted with the silica in solution, yielding its quota of K_2O , this reaction being more or less complete. Some of the KCl may have reacted and supplied some K_2O , part may have remained in solution as KCl , and the remainder may have been volatilized.

Second: Bearing in mind the first probability, there was evidently considerable variation in the composition of the Russian potash which might account for some of the melts showing opacity.

Third: We have found that a considerable amount of alkali may be lost by volatilization and that the amount varies with furnace conditions. This might also account for the erratic results secured when the proportions are so near a supersaturated solution.

A case is cited by the authors in which melts were made in two pots in the same furnace, one producing milky and the other clear glass. The respective content of SO_3 is stated to have been 0.10 per cent and 0.05 per cent, respectively—the Cl content being the same in each melt. It is remarkable if such a slight difference could possibly account for the conditions of opalescence—I feel that some other reason must be found to adequately explain it.

I feel convinced that, in the case of the borosilicate crown and dense flint glasses to which I referred, the milkiess was due to a deficiency of alkali—due to volatilization caused by improper melting conditions. I suspected that the arsenic was responsible for the cloudiness but subsequent melts in which a larger amount was used in the batch did not develop it. In one of our early experiments an excessive amount of arsenic was introduced by mistake and a dense white glass resulted. This

was also probably due to the formation of a supersaturated solution of silica on account of the fixation of a portion of the alkali by arsenic.

I have never found that the presence of SO_3 , Cl or F in soda-lime glass (in amounts up to 0.6 per cent of each) caused opalescence to the slightest extent, so long as the ratio of alkali to silica was below the limit at which opalescence occurs when SO_3 , Cl or F are absent.

In the case of opal glasses, such as the so-called Carrara glass, fluorine is generally used in some form, but its efficiency in producing opacity seems to depend on both the form in which it is introduced and the ratio of alkali and other bases to the silica. It has never to my knowledge been positively proven whether the opacity in this case is due to separated silica or to some fluorine compound.

I do not wish to convey the impression that the authors are incorrect in concluding that the presence of SO_3 and Cl in some optical glasses will cause milkiness, but simply to suggest that before this can be accepted, further experimentation is necessary. However, I believe it is very probable that the presence of salts in solution in glasses which contain a high proportion of silica (approaching a supersaturated solution) will tend to cause such glasses to more readily turn milky on slow heating or cooling.

PITTSBURGH PLATE GLASS COMPANY,
CREIGHTON, PA.

REPLY TO F. GELSTHARP'S DISCUSSION,

By C. N. FENNER AND J. B. FERGUSON.

We are very glad that Mr. Gelstharp has brought up for consideration the possibility that the opalescence or milkiness which we have described was caused by a deficiency of alkali. This is a reasonable hypothesis and deserves careful consideration, but the evidence does not seem to us to support it. We wish, however, to emphasize again the statement which we made in the original article, that we do not intend the explanation there offered to be understood to apply to all cases of milkiness or devitrification in glasses. It is only reasonable to suppose that a deficiency of alkali in a glass would be a contributory cause, and under some circumstances might be the most important

cause leading to devitrification. Nevertheless, we are strongly of the opinion that many glasses are somewhat supersaturated with silica and still do not ordinarily turn milky or devitrify, but that other factors may come in which exert controlling influences and lead to this result.

In what follows we wish to restrict ourselves to the phenomena which we discussed, and to give reasons why Mr. Gelstharp's interpretation does not seem to apply.

1. A suggestion is made as to the manner in which the use of a potash carrying SO_3 and Cl might lead to a deficiency in alkali. This is based upon a perhaps natural assumption as to the manner in which we allowed for the presence of these ingredients in our calculations, but as a matter of fact the procedure that we followed had a tendency to increase rather than decrease the percentage of alkali.

As we have mentioned, the maximum SO_3 content of Armour potash which it was considered judicious to tolerate for the light flint glass was 0.30 per cent, and with even this amount there was found to be a tendency toward the production of milkiness. That this was not due to a deficiency in alkali is shown by a consideration of the method used in adjusting our calculations. This was as follows: Since there is no reason to suppose that the K_2O content of K_2SO_4 in a lead-alkali-silica mixture is more volatile than the K_2O of K_2CO_3 , its equivalent in terms of K_2CO_3 was calculated and used as such if the K_2SO_4 content was large, but if it was only 0.20–0.30 per cent (as was generally the case) it was believed that no essential difference in the glass would be made by reckoning the K_2SO_4 as K_2CO_3 without conversion. The effect of this, as regards the composition of the glass, was almost imperceptible, as the following calculation shows:

Suppose the raw potash contains 80 per cent anhydrous K_2CO_3 and 1 per cent K_2SO_4 (equivalent to 0.46 per cent SO_3).

If all the K_2SO_4 were called K_2CO_3 , this would make 81 per cent K_2CO_3 in the raw potash, and to get 68 kg. of anhydrous K_2CO_3 in the batch 83.95 kg. of raw potash would be used. This would be supposed to contain 46.376 kg. of K_2O . Taking account of the K_2SO_4 , however, the 83.95 kg. of raw potash would actually contain 45.803 kg. of K_2O from carbonate and 0.454

kg. of K_2O from sulphate, or a total of 46.257 kg. of K_2O instead of 46.376 kg.

A batch of the kind under consideration would yield about 590 kg. of glass. The percentage of K_2O in the glass in the two cases would be

$$(a) \quad 46.257 \div 590 = 7.84 \text{ per cent.}$$

$$(b) \quad 46.376 \div 590 = 7.86 \text{ per cent.}$$

That is, the error (deficiency) arising from considering the K_2SO_4 as K_2CO_3 would amount to 0.02 per cent K_2O in the final glass, an insignificant amount.

KCl was treated differently. Data on what happens to KCl in a batch of this kind are very meager, but as we know that KCl is highly volatile, and as the amount was small, it seemed safest to consider that *all* of it escaped and not consider it a source of K_2O at all. Possibly some objection might be raised to this procedure but the reason for it would be the converse of that which Mr. Gelstharp has suggested. If any of the KCl did become converted into a K_2O compound and remain in the melt, the effect was to *raise* the K_2O content.

2. Mr. Gelstharp speaks of the probability that the glasses approach a supersaturated solution, and there seems to be an implication here that, as regards composition, they are in a critical region and that a little addition of silica will throw them over into a condition of supersaturation, causing a precipitate of silica to appear. We hesitate to believe that such is the state of affairs. We are rather inclined to think that all glasses of the type under discussion are somewhat supersaturated at 950–1000° C¹ and that a few tenths per cent increase or decrease in silica has no effect. A certain set of laboratory experiments which we have lately carried out gives evidence on this and other points.

A glass which became milky on reheating was used as the basis for the experiments.

Experiment 1. Several chunks of glass were placed in a platinum crucible and heated for about an hour at 950–1000° C. The

¹ Necessarily a definite temperature must be expressed; otherwise supersaturation has no meaning. We have taken a temperature at which latent milkiness is developed on reheating.

glass was cooled and broken out. It appeared very milky; even small pieces, 2-3 mm. in size, showed very perceptible opalescence.

Experiment 2. Another sample of the same glass was ground to pass 80 mesh and heated as follows:

1.50 P.M.	1410° C	2.15 P.M.	1490° C
3.45 P.M.	1482° C	4.10 P.M.	1494° C

The glass, cooled quickly, was perfectly clear. To determine whether milkiness could be developed it was reheated as follows:

10.45 A.M.	916° C	11.22 A.M.	1020° C
12.08 P.M.	996° C	1.20 P.M.	1008° C

It was then removed and cooled. The conditions were the optimum for developing milkiness, but none appeared. On the surface there was a thin film of white, devitrified material, but the bulk of the glass appeared perfectly clear.

Experiment 3. Another sample of the same glass as No. 1 was ground to pass 80 mesh and mixed thoroughly with 2 per cent of finely ground quartz. The heating was from 1400° C, at 2.25 P.M., to 1500° C at 4.18 P.M. It was cooled, and then reheated at 1018-1042° C for about three hours. After this treatment the surface devitrification was a little greater than in Experiment 2, but the material underneath the surface appeared to be wholly free from milkiness or other form of devitrification.

From these experiments we infer that the original sample of glass contained some ingredient which assisted the excess silica to crystallize out and thereby milkiness was produced, but that when this glass was heated to approximately 1500° C this ingredient was volatilized, and the glass, although still supersaturated with silica at 950-1000° C, thereby lost its power to free itself of excess silica. This result can hardly be attributed to a change in alkali produced by the high temperature, for any change of this sort would certainly be in the direction of a decrease rather than an increase in alkali.

3. Although laboratory experiments of this kind tend to support our conclusions, we do not attach nearly so much importance to them as to the large-scale experiments which the commercial operations represent. These showed the striking fact that when proper measures were taken to maintain the furnace temperatures at the desired level, the appearance of pots of milky glass ceased immediately, and for months following, trouble of this kind was practically negligible.

It is difficult to understand how this procedure can be supposed to cause more of the somewhat volatile alkalis to be retained in the melts, but it is easy to see that it would tend to drive out the last traces of any such materials as SO_3 or Cl .

Before making the changes in methods of temperature-control which we have described, Mr. Victor Martin, then chief glass-maker at the Bausch and Lomb plant and a man of wide experience in practical glass-making, had expressed the opinion that the trouble arising from milkiness could be obviated if it were possible to operate the furnaces at a higher temperature. Later experience showed that this was essentially true but that it was only necessary to keep the temperature at a point very little above that which we had believed to be suitable for ordinary conditions but which at times was not attained because of deceptive thermoelement indications.

Mr. Gelstharp refers to certain observations of his on the effect of arsenic in producing milkiness. He believes that the arsenic fixes a certain amount of alkali and thereby increases the amount of uncombined silica. Even if this be true, the amount of alkali which can reasonably be supposed to combine with the small amount of arsenic which is sufficient to produce milkiness is so small as to be practically negligible. To us it seems at least as reasonable that the action of arsenic is similar to that which we have assigned to SO_3 and Cl .

A criticism which seems to us applicable to Mr. Gelstharp's point of view is that in drawing his conclusions he does not make sufficient distinction between the amount of SO_3 , Cl and As which is put into the melt and that which stays in. All of these materials, in whatever form they are added, tend to be volatilized at high temperatures, and the statement that in certain cases

a relatively large amount of one or the other went into the melt without producing milky glass has, of itself, little bearing upon the question. We need to have in addition fairly complete information on the subsequent heat treatment or an analysis of the glass.

Although we agree with Mr. Gelstharp that final proof of our contention has not been obtained, nevertheless the evidence in that direction appears to us very strong, and no other explanation appears to meet the requirements.

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HEAT BALANCE ON A PRODUCER-GAS FIRED CHAMBER KILN.

By R. K. HURSH, Urbana, Ill.

The data presented here are based on tests made at the plant of the Baker Clay Company at Grand Ledge, Michigan, in the summer of 1917. The equipment tested consisted of a kiln of sixteen chambers, each having a capacity of fifty to fifty-five thousand standard sized brick, and three six-foot, water-sealed gas-producers of the pressure type.

The producers were connected by a header with the main gas-duct leading to the kiln. Each producer was equipped with a blower of the injector type using steam at pressures ranging from fifteen to forty pounds (gauge). A Virginia lump coal in sizes up to four inches was fired in charges of one hundred and fifty to two hundred pounds to each producer at hourly intervals.

Air for combustion in the kiln was drawn through the open doors and crown holes several chambers back of the one on fire and the combustion gases were passed through three heating chambers before delivery to the stack flue. No use was made of the usual water-smoking flues on the top of the kiln. The average firing period was forty to forty-four hours, the finishing temperature being 1075°C (1970°F.) in the top of the chamber.

Tests.

Coal was weighed separately for each producer and an average sample was reserved for analysis. Ashes were removed from the pits every other day and a sample was taken for analysis. Both analyses were made by J. M. Lindgren at the Chemistry Dept. of the University of Illinois.

The steam pressure at the blowers of the producers were taken at hourly intervals and the diameter of the orifice in the blower was measured. From the average pressure and the area of the orifice, the steam consumption was calculated by means of the

Grashof¹ formula. The use of a steam meter and a throttling calorimeter to determine the quality of the steam would have been desirable, but these were not available at the time. Since the pressure of the steam was reduced through a valve before reaching the gauge and the needle-valve at the orifice, it was assumed that the steam was saturated at the pressures read. Under the conditions this would not be greatly in error.

Samples of the hot producer-gas were collected through a glass lined sampling tube inserted in the gas-main a short distance from the header. The tube projected into the main to a point estimated to represent the mean velocity of gas flow. The gas was collected in glass containers over water saturated with the gas. To obtain an average sample of the gas, the sampling period extended over a time of one hour, or from one firing of the producers to the next. Analyses were made by means of a portable Burrell apparatus, CO₂, O₂, unsaturated hydrocarbons (considered as C₂H₄), CO, H₂, CH₄ and N₂ (by difference) being determined. Owing to the difficulties of accurate sampling and analysis, no attempt was made to determine the soot and tar. The losses due to separation of these in their passage through the ducts to the firing chamber were therefore accounted for in the item of general losses.

The temperature of the producer-gas was measured at the point of sampling by means of a base metal thermocouple encased in an iron tube.

The temperature and humidity of the atmospheric air were determined by means of wet and dry bulb hygrometer readings.

Temperatures in the tops of the kiln chambers were measured by means of a platinum-platinum-rhodium thermocouple inserted through the crown holes. These readings did not represent the average temperatures of the ware in the chambers but gave a measure of the rise in temperature during the test except in the last chamber through which the combustion gases passed. There the average rise in temperature of the ware was necessarily estimated from the data obtained.

Flue-gas samples were taken from the main draft flue near the point of delivery from the kiln. An iron sampling tube was in-

¹ Marks, "Mech. Engrs. Handbook," p. 354.

served with the end opening at the point of approximately mean gas velocity. With the low temperatures of the flue-gases, it was considered safe to use an iron tube for this purpose. The temperature was measured at the same point with a silver-constantan thermocouple.

An attempt was made to determine the average velocity of the flue-gases in the main draft flue by means of a Pitot tube, but the manometer was not sufficiently delicate to give satisfactory readings. The volume of flue-gas was therefore calculated from its analysis, from the analysis of the producer-gas, and from the weight of coal fired.

The test covered the period of firing one chamber—forty-four hours from the time the fires were started in it until its finish and the beginning of firing in the next chamber. Data on the firing of several chambers indicated that this test might be considered as fairly representative of the kiln operation.

CALCULATIONS.

Producer.

Volume of Producer Gas.—The weight of carbon consumed per kg. of coal fired was the carbon in the coal less that in the ashes, or $0.7437 - \frac{0.1052 \times 0.0472}{0.8028} = 0.7375$.

The carbon per cu. m. of producer-gas was:

$$\text{CO}_2 = 4.02\% = 0.0402$$

$$\text{C}_2\text{H}_4 = 0.6\% = 0.012$$

$$\text{CO} = 22.5\% = 0.225$$

$$\text{CH}_4 = 1.4\% = 0.014$$

$$\frac{0.2912}{22.4} \times \frac{12}{22.4} = 0.156 \text{ kg. per cu. m. of gas}$$

$$\frac{0.7375}{0.156} = 4.73 \text{ cu. m. producer-gas per 1 kg. of coal fired.}$$

Volume of Dry Air Used.—The N_2 content of the producer-gas furnished a measure of the amount of air used in the producer.

$$0.6348 \times 4.73 = 3.005 \text{ cu. m. N}_2 \text{ in gas per 1 kg. of coal.}$$

$$0.0139 \times \frac{22.4}{28} = 0.011 \text{ cu. m. N}_2 \text{ in gas from 1 kg. of coal.}$$

$$2.994 = \text{cu. m. N}_2 \text{ in gas from air used per 1 kg. of coal.}$$

$$\frac{2.994}{0.79} = 3.79 \text{ cu. m. dry air used per kg. of coal (at N. T. P.).}$$

$$3.79 \times 1.293 = 4.9 \text{ kgs. dry air used per kg. of coal.}$$

The average temperature of the atmospheric air was 17.5°C and the average moisture content was 0.00801 kg. per kg. of dry air. The total moisture entering the producer with the air was:

$$4.9 \times 0.00801 = 0.039 \text{ kg. per kg. of coal}$$

Steam Used in Producers. $M = 0.0165 F p^{.97}$ (Grashof).

M = lbs. steam flowing per second.

F = area of orifice in sq. ins. = 0.0276.

p = absolute pressure of steam in lbs. per sq. in.

Multiplying M by 3600 gave the weight of steam per hour, and dividing the total for the three producers by the average weight of coal fired to the three per hour gave the weight of steam in lbs. per lb. of coal, or in kgs. per kg. of coal.

$$\text{Producer 1. } M = 0.0165 \times 0.0276 \times 35.5^{.97} \times 3600 = 52.3$$

$$\text{Producer 2. } M = 0.0165 \times 0.0276 \times 34.4^{.97} \times 3600 = 50.7$$

$$\text{Producer 3. } M = 0.0165 \times 0.0276 \times 32.2^{.97} \times 3600 = 30.0$$

133.0

$$\frac{133.0}{468.5} = 0.284 \text{ lb. steam per lb. coal or kgs. steam per kg. of coal.}$$

The moisture entering the producers from the moisture and combustion of the hydrogen in the coal was:

$$0.0258 + 0.039 \times 9 = 0.377 \text{ kg. per kg. of coal}$$

The total moisture entering the producers from all sources was:

$$0.039 + 0.284 + 0.377 = 0.700 \text{ kgs. per kg. of coal fired}$$

Free Moisture in Producer-Gas.—The difference between the total moisture entering the producers and the moisture equivalent to the free and combined hydrogen in the gas represents the free moisture in the gas.

$$\text{H}_2 = 7.5\% = 0.075 \text{ cu. m. H}_2\text{O vapor per cu. m. gas (at N. T. P.)}$$

$$\text{C}_2\text{H}_4 = 0.6\% = 0.012 \text{ cu. m. H}_2\text{O vapor per cu. m. gas (at N. T. P.)}$$

$$\text{CH}_4 = 1.4\% = \frac{0.028}{0.115} \text{ cu. m. H}_2\text{O vapor per cu. m. gas (at N. T. P.)}$$

0.115

$0.115 \times 4.73 = 0.544$ cu. m. H_2O vapor equivalent to H_2 in gas per kg. of coal, or $0.544 \times 0.804 = 0.437$ kg.

$0.700 - 0.437 = 0.263$ kg. free moisture in gas per kg. coal fired.

Calorific Value of Producer-Gas from Analysis.

$$C_2H_4 = 0.6\% = 0.006 \times 12915 = 77.5$$

$$CO = 22.5\% = 0.225 \times 3044 = 684.9$$

$$H_2 = 7.5\% = 0.075 \times 2594 = 194.5$$

$$CH_4 = 1.4\% = 0.014 \times 8558 = 119.8$$

$$1076.7 \text{ Cals. per cu. m. gas}$$

$$1076.7 \times 4.73 = 5095 \text{ Cals. per kg. of coal fired.}$$

Sensible Heat of Producer-Gas.—The average temperature of the producer-gas was $575^\circ C$. The average specific heats were obtained from the formulas of Langen.¹

$$CO_2 = 4.02\% = 0.0402 \times (0.39 + 0.00012 \times 575) \times 575 = 10.6$$

$$CH_4 = 1.4\% = 0.014 \times (0.34 + 0.00036 \times 575) \times 575 = 4.4$$

$$C_2H_4 = 0.6\% = 0.006 \times (0.42 + 0.00049 \times 575) \times 575 = 2.4$$

$$\left\{ \begin{array}{l} H_2, CO \\ O_2, N_2 \end{array} \right\} 93.98\% = 0.9398 \times (0.31 + 0.000027 \times 575) \times 575 = 175.7$$

$$\text{Sensible heat per cu. m. of dry gas} = 193.1 \text{ Cals.}$$

$$193.2 \times 4.73 = 914 \text{ Cals. per kg. of coal fired.}$$

$$0.263 \text{ kg. } H_2O \text{ vapor, } 0.263 \times (0.44 + 0.000012 \times 575) \times 575 = 77 \text{ Cals.}$$

The total sensible heat in the moist producer-gas per kg. of coal is $914 + 77 = 991$ Cals.

The total heat content of the hot producer-gas was:

$$5095 + 991 = 6086 \text{ Cals. per kg. of coal fired}$$

Heat Input for Producers.—The heat content of the dry air supplied to the producers at the average temperature, $17.5^\circ C$, was:

$$4.9 \times 0.241 \times 17.5 = 20.8 \text{ Cals. per kg. of coal fired}$$

The heat content of the moisture in the atmospheric air at average conditions was:

$$4.9 \times 0.00801 \times 604 = 23.7 \text{ Cals. per kg. of coal fired}$$

¹ Marks, "Mech. Engr. Handbook," p. 366.

The total heat in the atmospheric air supplied was 44.5 Cals per kg. of coal.

The heat content of the steam supplied to the blowers, assuming it to be saturated at the average pressure, was:

$$0.284 \times 644 = 183 \text{ Cals. per kg. of coal fired.}$$

The calorific value of the coal was 7108 and the total heat input to the producers was $7108 + 183 + 44.5 = 7335$ Cals. per kg. of coal.

The Hot Gas Efficiency was $\frac{6086}{7335} = 82.97$ per cent.

Heat Lost in Unburned Carbon in Ashes.—The amount of unburned carbon in the ashes in terms of weight of coal was:

$$\frac{0.0472 \times 0.1052}{0.8028} = 0.0062 \text{ and the heat value, } 0.0062 \times 8100 = 50 \text{ Cals. per kg. of coal fired.}$$

Undetermined Heat Losses.—The heat losses due to conduction, radiation, etc., were determined by difference.

$$7335 - (6086 + 50) = 1199 \text{ Cals. per kg. of coal fired.}$$

Kiln Data.

Volumes of Flue-Gas and Air Used in Kiln.—The CO_2 from combustion of the producer-gas amounted to 2.9 per cent by volume of the flue-gas. The volume of CO_2 from the producer-gas was:

$$\begin{aligned} \text{CO}_2 &= 4.02\% = 0.0402 \\ \text{C}_2\text{H}_4 &= 0.6\% = 0.012 \\ \text{CH}_4 &= 1.4\% = 0.014 \\ \text{CO} &= 22.5\% = 0.225 \end{aligned}$$

$$0.2912 \text{ cu. m. CO}_2 \text{ per cu. m. producer-gas}$$

$$\frac{0.2912}{0.029} = 10.04 \text{ cu. m. flue-gas per cu. m. producer-gas.}$$

The N_2 in the flue-gas amounted to 79.3 per cent or $0.793 \times 10.04 = 7.962$ cu. m. per cu. m. producer-gas. Of this amount 0.6348 cu. m. was from the producer-gas and $7.962 - 0.6348 = 7.33$ cu. m. was from the air supplied in the kiln. The volume of air furnished was:

$$\frac{7.33}{0.79} = 9.28 \text{ cu. m. (at N. T. P.) per cu. m. of producer-gas.}$$

The total volume of flue-gas during the period of the test was

$$9371 \times 4.73 \times 10.04 = 445,000 \text{ cu. m. (at N. T. P.)}$$

The total volume of dry air supplied to the kiln was

$$9371 \times 4.73 \times 9.28 = 411,300 \text{ cu. m. (at N. T. P.)}$$

The weight of moisture introduced with the air supplied to the kiln was $411,300 \times 0.00801 \times 1.293 = 4260 \text{ kgs.}$

Sensible Heat of Flue-Gas.—The sensible heat of the flue-gas, calculated by the use of the Langen formulas for average specific heat, was:

$$\text{CO}_2 \quad (0.029 \times 445,000) \times 0.21 \times 170 \times \frac{44}{22.4} = 1,140,000 \text{ Cals.}$$

$$\text{O}_2 \quad (0.178 \times 445,000) \times 0.217 \times 170 \times \frac{32}{22.4} = 4,175,000 \text{ Cals.}$$

$$\text{N}_2 \quad (0.793 \times 445,000) \times 0.247 \times 170 \times \frac{28}{22.4} = 18,530,000 \text{ Cals.}$$

$$\text{Sensible heat of dry flue-gas} = 23,845,000 \text{ Cals.}$$

The total moisture in the flue-gas from the air used in the kiln and from combustion of the producer-gas was:

$$4260 + 9371 \times 0.700 = 10,820 \text{ kgs. Its heat content at the average temperature of the flue-gas was } 10,820 \times 0.46 \times 170 = 845,000 \text{ Cals.}$$

The total heat in the flue-gas was therefore 24,690,000 Cals.

Heat Used for Burning the Ware.—During the test the temperature was raised in four chambers of the kiln. The heat used in each chamber for raising the temperature of the clay was calculated separately. In one chamber the chemical water in the clay was expelled—requiring expenditure of heat—and some carbon contained in the clay was consumed. The heat from the latter was added to the other items of heat input for the kiln. In the last chamber some mechanically held moisture was expelled.

Since the temperature of the flue-gases leaving the kiln was considerably lower than that at which either the hygroscopic or chemical water in the clay was expelled, the heat content of

the steam from both sources was represented by the heat in superheated steam at the temperature of the flue-gases and at the existent vapor pressure. This value was obtained from Goodenough's steam tables.

In the case of chemically combined water, the heat required at dissociation would be that required for the endothermic reaction plus the latent heat of vaporization of steam at the dissociation temperature. In the dehydration of clay, the temperature of dissociation is above the critical temperature of water and the latent heat of vaporization would hence be zero. However, it must be considered that, in heating up the clay to the dissociation temperature, the moisture in the clay has taken up an amount of heat equivalent to the heat content of steam at the temperature and pressure existent at the point of dissociation. Hence, the use of formulas for the latent heat of vaporization of steam at dehydration temperatures of clays is not strictly correct.

Various values are given for the heat of dissociation of clay. Bleininger¹ used an assumed value of 200 Cals. per kg. of water expelled. Harrop² used a value, 609, from a formula given by Richards. Tschernobaëff³ determined a value of 112 Cals. per kg. of pure kaolinite. Mellor and Holdcroft,⁴ by graphical calculation from lag curves, found 42 Cals. per kg. of clay for the endothermic reaction at dehydration and 21.5 Cals. for the exothermic reaction at about 1000° C. From lag curves given by Brown and Montgomery,⁵ approximate calculations gave values ranging from 757 to 1015 Cals. per kg. of water for clays having 10.7 to 13.2 per cent chemical water. As would be expected, the heat required increases with the amount of chemical water in the clay. On the basis of these data the value for the clay in this test, containing 4.65 per cent chemical water, was taken as 220 Cals. per kg. of chemical water.

The heat required to raise the temperature of the clay in the respective chambers was:

¹ A. V. Bleininger, *Trans. Am. Ceram. Soc.*, **10**, 417 (1908).

² C. B. Harrop, *Ibid.*, **14**, 227 (1912).

³ D. Tschernobaëff, *Rev métal.*, **1905**, p. 729.

⁴ Mellor and Holdcroft, *Trans. Eng. Ceram. Soc.*, **10**, 101.

⁵ Brown and Montgomery, *Trans. Am. Ceram. Soc.*, **14**, 711 (1912).

$$\text{Chamber 10. } 53,320 \times 2.5 \times 0.23 \times 210 = 6,438,000$$

$$\text{Chamber 11. } 54,560 \times 2.5 \times 0.23 \times 300 = 9,412,000$$

$$\text{Chamber 12. } 54,560 \times 2.5 \times 0.23 \times 180 = 5,649,000$$

$$\text{Chamber 13. } 52,080 \times 2.5 \times 0.20 \times 300 = 9,832,000$$

$$\text{Heat for clay} = 31,331,000 \text{ Cals.}$$

The mechanically held water was expelled in Chamber 13, requiring $52,080 \times 2.5 \times 0.014 \times 631.2 = 1,073,000$ Cals. in the steam at the flue-gas temperature.

The chemical water was expelled in Chamber 12. The heat required for dissociation was 220 Cals. per kg. of water. The heat in the steam at the flue-gas temperature was 631.2 Cals. The heat requirement was then 851.2 Cals. per kg. of water. But the ware in Chamber 12 was at an average temperature of 300°C at the beginning of the test and the chemical water in the clay at the time was assumed to have held the heat equivalent to that of steam at the same temperature, 715 Cals. per kg. The actual amount of heat required for the chemical water was, hence, 136 Cals. per kg.

$$54,560 \times 2.5 \times 0.0465 \times 136 = 863,000 \text{ Cals.}$$

The total heat required for the ware during the test was 33,267,000 Cals.

Heat Input for Kiln.—The heat value of the hot producer-gas, the heat in the atmospheric air supplied to the kiln, and the heat from combustion of carbon in the clay constituted the heat input.

The heat in the producer-gas was $9371 \times 6086 = 57,032,000$ Cals.

The heat content of the atmospheric air, as supplied to the producers, was 44.4 Cals. per 3.79 cu. m. of dry air per kg. of coal or 11.72 Cals. per cu. m., including the heat in the moisture. The air supplied to the kiln furnished $411,300 \times 11.72 = 4,819,000$ Cals.

The heat from the combustion of 0.25 per cent of carbon in the clay in Chamber 12 furnished $54,560 \times 2.5 \times 0.0025 \times 8,100 = 2,762,000$ Cals.

The total heat input for the kiln alone was 64,613,000 Cals., of which 33,267,000 Cals. were used for burning the ware (51.49 per cent), 26,690,000 Cals. were lost in the flue-gas (38.21 per cent)

and the balance, 6,656,000 Cals. (10.30 per cent) were charged to conduction, radiation and other undetermined losses.

Considering the kiln and producers as a unit, the total heat input from coal fired, air supplied to producers and kiln, steam supplied to the producers and carbon in the clay was 76,318,000 Cals. Of this amount, 43.59 per cent went to the burning of the ware, 32.35 per cent to the flue-gas, 8.72 per cent to heat losses from the kiln, 14.72 per cent to heat losses from the producers and 0.62 per cent loss was due to unburned carbon in the ashes. The data for the combined unit, together with the heat

FIG. 1.

HEAT BALANCE CHART.

HEAT BALANCE OF GAS PRODUCERS.

Total heat input from coal, air and steam	100 %
Heat in producer gas, calorific value plus sensible heat	82.97 %
Loss due to conduction, radiation, etc.	10.35 %
Loss due to unburned carbon in ashes	0.68 %

HEAT BALANCE OF KILN

Total heat input from producer gas, air and carbon in clay	100 %
Heat to raise temp. of clay and drive off water	51.49 %
Loss due to sensible heat of flue gas	38.21 %
Loss due to conduction, radiation, etc.	10.30 %

HEAT BALANCE OF KILN AND PRODUCERS COMBINED.

Total heat input from coal, air, steam and carbon in clay	100 %
Heat to raise temp. of clay and drive off water	43.59 %
Loss due to sensible heat of flue-gas.	32.35 %
Loss due to conduction, radiation, etc from kiln	8.72 %
Loss due to conduction, radiation, etc from producers.	14.72 %
Loss due to unburned carbon in ashes.	0.62 %

distribution for producers and kiln separately, appear on the accompanying chart.

Discussion of Results.

The data, as presented, serve as a means of comparing the heat distribution in a kiln of this type with that in periodic kilns used for similar products. As would be expected, the losses to be charged to conduction and radiation are much reduced, since a considerable amount of the heat going to the kiln structure during the firing period was recovered during the cooling—preheating the air for combustion. Hence, the percentage of the heat input which may be charged to the burning operation is much increased over that of the periodic kiln.

Of the heat charged to the heating up of the clay, the greatest portion was actually lost from the kiln by radiation and conduction and in the heat in outgoing ware. However, since it was first applied to the ware to accomplish the burning operation, it was properly charged thus.

Although the temperature of the outgoing flue-gas was very low, the large excess of air admitted to the kiln resulted in a large volume of flue-gas and, consequently, a large loss of heat in the flue-gas. If some means of regulating the amount of air admitted were applied, this loss could be materially reduced.

It would be of interest to determine the actual amount of heat lost from the kiln structure itself and that remaining in the burned ware and which escaped to the atmosphere by circulation of the air through the cooling chambers and through the openings in the crown and the doorways. Considerable difficulty would have been encountered in obtaining the necessary data for this purpose.

In conclusion, the writer desires to express his indebtedness to Prof. C. W. Parmelee for his able assistance in carrying out the tests, to Mr. C. W. Parks who assisted in obtaining some of the data, and to the Baker Clay Company and the International Clay Machinery Company for their coöperation in the work.

SOME FACTORS INFLUENCING THE TIME OF SET OF CALCINED GYPSUM.¹

By F. F. HOUSEHOLDER.

Introduction.

The time of set calcined gypsum is one of its very important properties. Several methods for its measurement have been suggested and the chief ones have been tested and rated according to their merits.² However, no data resulting from thorough work on the relation of the time of set to the other physical properties is available. Obviously, this relation will depend upon the purity of the gypsum from which the plaster is made, the temperature at which it is calcined, and the amount of retarder or accelerator added. Experience shows that it also depends upon the cleanliness of the boxes or vessels in which the plaster is mixed, and the purity of the water used.

This preliminary note describes some tests made in order to determine the effect of varying the consistency of the mixtures, the time of stirring, the rate of stirring, and the temperature of the water used in mixing, on the time of set of calcined gypsum. The tests reported—although they may be of some value in themselves—were made as a guide in outlining further and more extensive tests on the physical properties of gypsum.

Preparation of Samples.—The same grade of plaster was used (without the addition of any retarder or accelerator) throughout the whole series of tests. A sample of 300 g. was made up in each case in a clean casserole. Each sample was stirred by means of a small spatula—kept well polished. The plaster was added to the water as rapidly as possible (4 to 5 seconds) without splashing or waste and allowed to stand undisturbed for one minute. It was then poured (or was stirred as the test demanded and then poured) into the standard mold of a Vicat³ apparatus. The

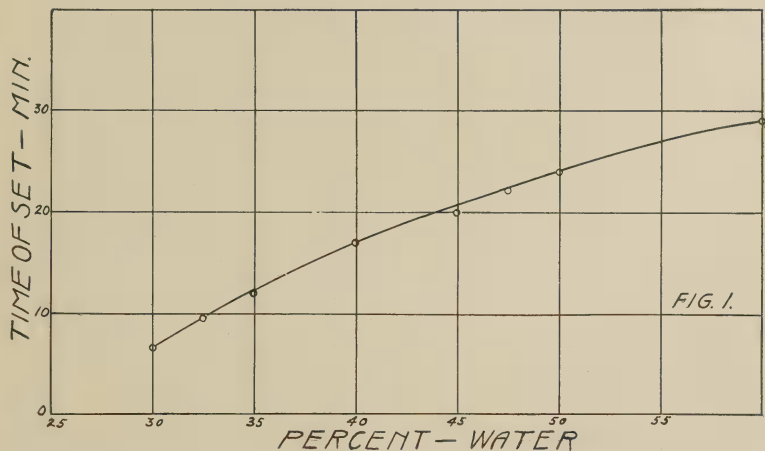
¹ By permission of the Director, Bureau of Standards.

² Emley, *Trans. Am. Ceram. Soc.*, **19**, 573-584.

³ 1915 Year Book, A. S. T. M., p. 359.

mold was thoroughly cleaned before each test and covered with a very thin coating of oil. The time of set was determined, as suggested by Emley,¹ by means of the standard Vicat needle.

Effect of Per cent Water Added.—To determine the effect of the amount of water used in mixing the plaster, on the time of set, samples containing 30, $32\frac{1}{2}$, 35, $37\frac{1}{2}$, 40, $42\frac{1}{2}$, 45, $47\frac{1}{2}$, 50 and 60 per cent of water, respectively, were made up and tested. A large number of tests on each mixture were made and the average results at each percentage plotted. In Fig. 1 is shown the variation in the time of set with the amount of water



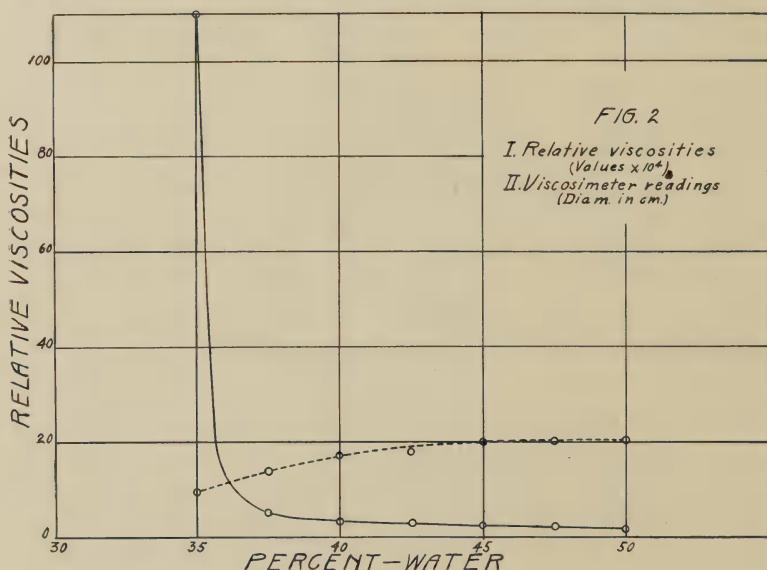
used in the mixtures. The samples containing 30 per cent water were so stiff and viscous that much care and effort were required in introducing them into the mold. However, the time of set of the individual samples did not vary from the average by more than one-half minute. The sample containing $32\frac{1}{2}$ per cent water was too viscous to mold satisfactorily, but gave fairly uniform values.

The curve (Fig. 1) shows a fairly uniform increase in the time of set as the percentage of water was increased until about 45 per cent was reached. Then the increase in time of set was less rapid—due to the fact that when the mixture was poured into

¹ See page 578, *Loc cit.*, 19, 583-4.

the mold the plaster settled to the bottom and the excess water came to the top. A thin film of water came to the top of the 47½ per cent sample, and in the case of the 50 per cent sample, a layer of water 1–1.5 mm. deep formed, while with the 60 per cent sample, the water was 7 mm. deep at the top of the mold. Evidently, before any setting had taken place, the mixture was reduced to about 47 or 48 per cent water and the further retardation was probably due, in part at least, to the fact that the plaster was under water. Also, the layer of water at the top of the mold increased the penetrating ability of the needle. These samples did not harden at the top—not even after the pouring off of the water and their removal from the mold. A day or two later the top could be brushed away with the hand. Considering the samples containing from 30 to 45 per cent water, an increase in the time of set from 6.5 minutes to 20 minutes, or approximately 300 per cent, is noted, while in the 45 to 60 per cent samples it increases from 20 minutes to 29 minutes or approximately 50 per cent.

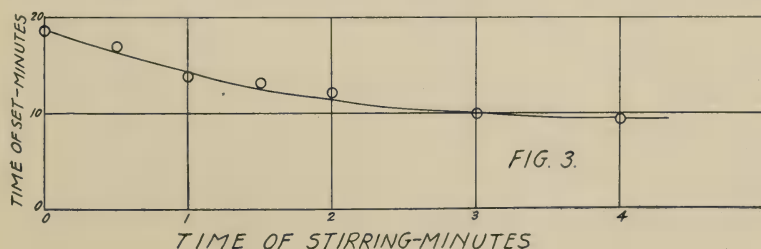
Viscosity Measurements.—The relative viscosities of each of the samples was determined by means of the Southard viscosi-



meter. The samples from 35 per cent up were placed in the viscosimeter and gave the results shown by the dotted curve (Fig. 2.). Assuming that the "patties" were circular, the viscosity of a mixture would vary inversely as the square of the diameter of the "patty." The relative viscosities are shown by the solid curve (Fig. 2). A very marked decrease is noted between the water contents of 35 and 40 per cent but not much change is noted thereafter. The instrument used was not water tight and hence the 60 per cent sample was not tested. The shape of the viscosity curve would indicate that the viscosity very rapidly approaches that of water and probably reaches it before it crosses the 100 per cent abscissa. Lack of data makes it unsafe to judge where the two curves meet.

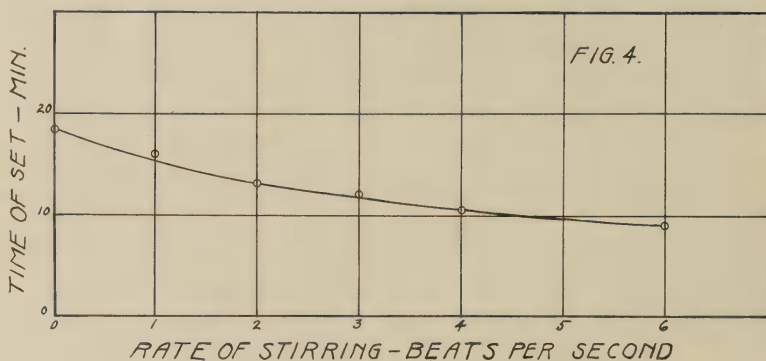
No extensive work has been published on the properties of gypsum solutions, although investigations along this line may lead to a more satisfactory definition of normal consistency. The immediate results obtained here indicate, that decreasing the viscosity increases the time of set, but that the relation between the two is not a simple function.

Effect of Stirring.—In determining the effect of continued stirring, the samples used were mixed with 40 per cent water and each was stirred with a small spatula at the rate of four strokes per second. The calcined gypsum was added to the water and the mixture allowed to stand one minute, as before. The first sample was then poured immediately into the mold and the time of set determined. Each of the others was stirred at the same rates for 0, 0.5, 1, 2, 3, and 4 minutes, respectively, and then poured into the mold. In Fig. 3 is shown the results of the tests. Continuous stirring for four minutes decreases the time of set from



18.5 minutes (with no stirring) to 9.5 minutes or to almost one-half. The general shape of the curve would indicate that the time of set would not be very greatly decreased by a continuation of the stirring.

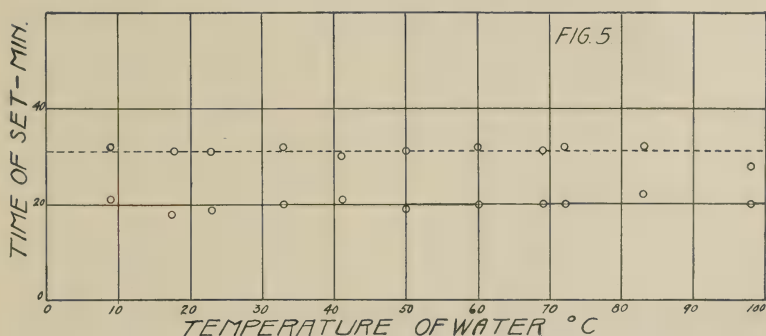
In Fig. 4 is shown the effect of varying the speed of stirring of the same kind of samples on the time of set. The stirring was all done by hand and the speed varied from 0 to 6 strokes per second (each sample being stirred for one minute only). In-



creased speed of stirring reduced the time of set. The shape of this curve is very similar to that of the curve shown in Fig. 3, although the decrease in the time of set is not so marked. The increased agitation of the mixture—either by increased stirring or by more rapid stirring—hastened the time of set. The first effect is probably to increase the rate at which the dry plaster takes up the water and goes into solution. The first crystal clusters formed are probably broken up and distributed throughout the mixture—thus becoming nuclei for further crystallization.

Effect of Temperature.—The effect of heating the water before mixing with the plaster was also tried out. The samples used for this purpose contained 40 per cent water and each was stirred at the same rate and for the same time as before. The data secured is less uniform than that secured in the foregoing experiments, but does not vary in any given direction. The conclusion reached is, that the temperature of the water has no appreciable

effect on the time of set. The setting of calcined gypsum is always accompanied by an evolution of heat (pure $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ in forming $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ giving up about 3700 cal. per gram molecular weight). Heating would therefore tend to retard the process were it kept confined. On the other hand, the solubility of calcined gypsum tends to increase with a rise in temperature of the water—which would probably induce an acceleration of the process. Evidently, from the results of this test, the two factors mentioned would about balance each other.



By the heavy curve (Fig. 5) is shown the time of set as determined by this test. The dotted curve shows the points at which the needle did not penetrate at all, or the time of hardening of the gypsum. The same regularity that is seen in the time of set is shown here.

Conclusions.

1. Increasing the proportion of water causes a decrease in viscosity and an increase in the time of set of calcined gypsum.
2. Vigorous and continuous agitation, when mixing the calcined gypsum with the water, tends to decrease the time of set.
3. The temperature of the water used in mixing has no influence on the time of set.

The above experiments were the outcome of the suggestions of Mr. C. A. Birdsley, Chief Engineer; P. H. Butler, Supt.; and J. A. Davis, of the Oakland Plant of the U. S. Gypsum Co. Acknowledgments are also due Mr. F. A. Kirkpatrick for many valuable suggestions in making the experiments.

THE NATURE OF THE AIR CONTENT OF PUGGED CLAYS.

BY H. SPURRIER.

As a sequel to some work done on the quantitative measurement of the air content of pugged clays, the question arose as to the composition of such air after imprisonment for a greater or less period in the clay body. A preliminary analysis of the liberated and collected gases gave an oxygen content of 7 per cent as against a normal oxygen content in free air of about 21 per cent.

At the time of this determination, it was not possible to secure a large enough sample to make a complete analysis that could be relied upon as thoroughly trustworthy. Recently, a very simple scheme (Fig. 1) was devised to secure any desired amount of the gas occluded in clay.

A large glass funnel was inverted and equipped with a tube of 30 millimeters internal diameter, suitably drawn out at both

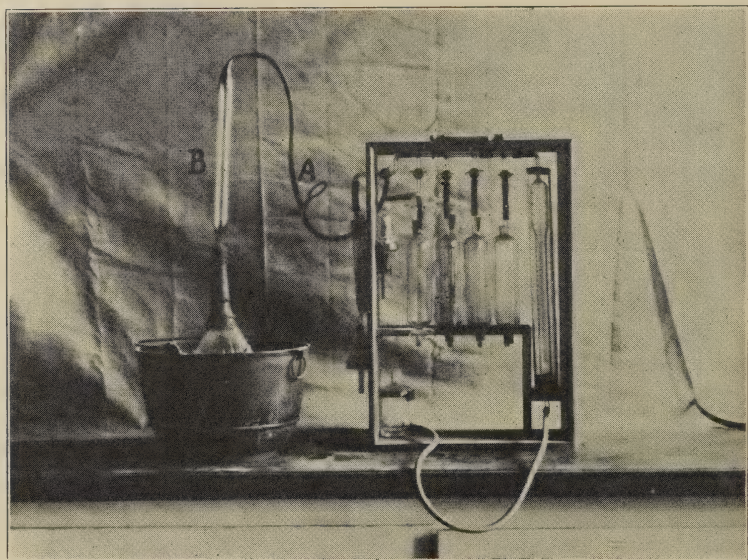


FIG. 1.

ends. The upper end was bent at a right angle and a gas-tight joint was made at the lower end between the tube and the inverted funnel. The funnel was then partly immersed in water contained in a large iron kettle. The water was boiled for a considerable time to eliminate dissolved gases, allowing steam to issue at the upper end for about 15 minutes. The screw-cock at "A" was then closed and the flame lowered till the water was just at the boiling point. The tube "B," on cooling, filled itself completely with water—proving the expulsion of the air.

Clay blanks which had been pugged about 24 hours previously were then slipped under the funnel; as the blanks disintegrated, the contained air was liberated—rising to the top of the tube "B." This was continued until a sufficient quantity of the gases had been collected.

The transfer and analysis of the gases needs no description. The following analysis represents the collected gases:

	Per cent.
Carbon dioxide.....	3.85
Oxygen.....	13.46
Carbon monoxide.....	1.92
Nitrogen.....	80.77
	<hr/>
	100.00

As is well known, if a bituminous coal is kept in a confined atmosphere, it will extract nearly all of the oxygen therefrom. As no further work has as yet been done, it would be somewhat hazardous to draw any conclusions as to what might be called the secondary effects of the change made obvious by the analysis. The aim of the present note is to bring the matter to your attention and to stimulate other workers in this direction. There are indications that the change is not quite so simple as at first sight might seem apparent, and that further investigation of the phenomenon might not be barren of results of practical importance.

It is obvious, of course, that these chemical changes are intimately connected with the well-known physical changes that take place during the ageing and weathering of clays. Some light might, in this way, be thrown upon the much studied and as yet imperfectly understood question of plasticity.

ACTIVITIES OF THE SOCIETY.

This department has been established by the Publication Committee, at the request of the President, in order to keep the membership in general informed of the activities of the officers, the Board of Trustees, and the several committees of the Society. This will be the official avenue of appeal to the membership for coöperation in the work of the Board and committees. Reports of the various Local and Student Sections will be published here and also accessions to membership, notice of death of members and other items of Society news. No personal items, unless they are also distinctly Society news, will be printed.

Next Annual Meeting.

The Board of Trustees has voted that the next annual meeting shall be held at the Fort Pitt Hotel, Pittsburgh, Pa., on February 3rd, 4th and 5th. Details will be published later.

Resolutions Passed by the Board.

Professional Divisions may be formed in the following ways:

1. "When the initiative in the formation of Divisions is taken by members who are interested, a petition may be presented by not less than ten members in good standing, of whom three or more shall be Active, who are interested especially in some phase of ceramic work sufficiently broad to warrant the formation of a special Division. This petition shall go to the President who shall then appoint a representative committee to consider the advisability of forming such a Division, and to proceed with the organization if the decision is favorable."
2. "When the initiative is taken by the Board of Trustees in order to stimulate the growth of the Society, the President shall appoint a representative man to furnish the initiative. He shall select his own committee."

The Board has passed a resolution to the effect:

"That fifty copies of each issue of the JOURNAL shall be assigned to the order of the Chairman of the Membership Committee, the number to be subject to reduction by the Board if the results do not seem to justify the expense."

Motions Pending.

Motion by Mr. Montgomery, for immediate decision:

"That the President shall appoint a representative individual for each Division to be organized, who shall select his own committee as provided in Section 2, of the motion recently passed by the Board for this purpose, and that these committees shall proceed to organize the following Divisions before our meeting in February:

1. Glass Division.
2. Enamel Division.
3. Pottery or White Ware Division, including porcelain.
4. Refractories Division.
5. Structural Clay Products Division.

With motion, by the President, to amend by striking out

5. Structural Clay Products Division
and adding:
5. Brick and Tile Division, including brick, hollow-tile and drain-tile.
6. Terra Cotta and Faience Division.
7. Abrasive Division."

Motions by the President, for decision December 20th.

1. "That the Committee on Publications be instructed to complete as soon as possible the "Index of the Transactions of the American Ceramic Society" and to submit to the Board of Trustees an estimate of the cost of publishing same."

2. "That no Local Section, Student Section or Division shall have the right to assess Section or Division dues against members of the parent Society, unless such members have signified their desire in writing to be considered members of said Section or Division."

3. "That, as of the date of November 1, 1918, fifty (50) copies of each volume of the Transactions be reserved for sale in complete sets only, and that the Secretary be instructed to purchase, at five dollars (\$5.00) each, sufficient copies to bring the total stock of each volume to that figure."

4. "That two hundred (200) copies of each number of the Journal be reserved at the time of issue for sale in complete sets only, and that an additional two hundred (200) copies be likewise reserved for sale in complete volumes only. Furthermore, that it is the sense of this resolution that a 'complete set' shall consist of the first five volumes of the Journal and such additional volumes as shall have been issued up to the date of the sale, and that a 'sale' shall be the actual selling of volumes and not the furnishing of them in consideration of payment of membership dues."

5. "That copies of the volumes of the Transactions and of the Journal shall be furnished to members who have or shall allow their dues to become delinquent only after the number reserved for sale has been provided. Furthermore, that in cases in which the volume that should be furnished in considera-

tion of a certain year's dues is not available, the member shall have the option of selecting any available volume or having the dues apply to the succeeding year."

Full discussion by the membership and suggestions in regard to these resolutions is desired by the Board. Any communications sent to the President or Secretary will be transmitted to the other members of the Board. They will not be published here. The President desires suggestions as to proper persons to appoint for the organization of the various Divisions.

ACQUISITION OF NEW MEMBERS DURING NOVEMBER, 1918.

Associate.

Frederick K. Minor, Celite Products Co., Pittsburgh, Pa.
John W. Yuill, Hercules Powder Co., Nitro, W. Va.
G. F. Dufour, Y. M. C. A., Hamilton, Ohio.
Melville Marks, Moore & Munger, New York, N. Y.
Dr. A. Bigot, 112 Avenue de Suffren, Paris, France.

Contributing.

Champion Ignition Company, Flint, Michigan.

LOCAL SECTION MEETINGS.

NORTHERN OHIO SECTION.

A joint meeting of the Northern Ohio Section of the American Ceramic Society and the Cleveland Section of the American Chemical Society was held in the Hotel Olmstead, Cleveland, Ohio, on December 9, 1918. The following program was afforded at the afternoon and evening sessions:

CERAMIC SECTION—AFTERNOON MEETING—3.00 P.M.

"Ceramic Features of the Chemical Exposition," by W. M. Clark, National Lamp Works, Cleveland, Ohio.

"Observations on the Apparent Cause of Failure of Lead-Glass Pots," by A. F. Gorton, Buckeye Clay Pot Co., Toledo, Ohio.

Discussion—"After-War Adjustments of the Ceramic Industries."

Business Session—By-laws and other important matters relative to the Local Sections.

CHEMICAL AND CERAMIC SECTIONS—JOINT MEETING—8.00 P.M.

"Refractory Materials as a Field for Research," by Dr. E. W. Washburn, National Research Council, Washington, D. C.

The meeting was a successful one in every way. It was better attended and even more interesting than the previous meetings which the Northern Ohio Section has held.

The paper by Mr. W. M. Clark was a very able review of the Ceramic features of the Chemical Exposition together with certain exceedingly interesting conclusions which Mr. Clark drew therefrom.

The paper by Dr. Gorton on "Causes of Failure of Lead-Glass Pots" was very instructive and promises to be of interest to readers of the Journal.

Mr. Stowe, in a paper on "Magnesite" (not mentioned in the formal program), ably discussed the recent developments in this important branch of the refractories industry.

The paper by Dr. Washburn at the joint meeting in the evening was a very interesting presentation of some of his impressions and findings as a member of the National Research Council. This paper will be published in an early number of the Journal.

R. D. LANDRUM, *Secretary*,
Cleveland Section,
American Chemical Society.

B. A. RICE, *Secretary*,
Northern Ohio Section,
American Ceramic Society.

NEW JERSEY CLAY WORKERS' ASSOCIATION.

A well attended meeting of the New Jersey Clay Workers Association was held at Rutgers College, New Brunswick, N. J., on December 17th. The following program was afforded at the morning and afternoon sessions:

MORNING SESSION.

"Some Defects in Terra Cotta," by D. F. Alberty, Federal Terra Cotta Co., Woodbridge, New Jersey.

"Sagger Mixtures," by Prof. G. H. Brown, Department of Ceramics, Rutgers College, New Brunswick, New Jersey.

"The Effect of Some Fluxes in Porcelain," by F. H. Riddle, Bureau of Standards, Pittsburgh, Pa.

AFTERNOON SESSION.

"Fuel Combustion," by Henry Kreisinger, Fuel Section of the U. S. Bureau of Mines, Pittsburgh, Pa.

"Future Kiln Developments," by Prof. Carl B. Harrop, Department of Ceramic Engineering, Ohio State University, Columbus, Ohio.

"Solving One of the Clay Manufacturers Greatest Problems," by Mr. Paul D. March, Philadelphia Textile Machinery Co., Philadelphia, Pa.

The New Jersey Clay Workers Association will apply for a charter as a Local Section of the American Ceramic Society at the annual meeting of the Society in February.

JOURNAL OF THE AMERICAN CERAMIC SOCIETY

A monthly journal devoted to the arts and sciences related to
the silicate industries.

Vol. 1

September, 1918

No. 9

EDITORIALS.

THE PATENT SITUATION.

A mode of relaxation available to any ceramist is the study of current patent specifications referring to inventions of a ceramic nature and which is certain to afford a constant source of amusement. Still, a feeling of apprehension is apt to creep over the unsophisticated follower of the fictile arts when he discovers that he is daily and unsuspectingly violating valuable privileges by making use of the common constituents of his products. For, have not patents been issued upon the employment of kaolin, feldspar and quartz in ceramic bodies? Indeed, this is not a jest but the solemn truth as may be readily proven by reference to the official lists. And what of the weird compositions of glasses, enamels and glazes to say nothing of the wonderful compositions of refractories, cement brick and other products which have been duly protected. Equally elevating is the perusal of the patent descriptions referring to kilns, driers, furnaces and other appliances employed in our art, some of which represent ideas hoary with antiquity.

Seriously speaking, the situation as regards ceramic patents is appalling. It is evident that our whole system of affording patent protection to inventions relating to our industries is without rhyme or reason. Like heaven's mercy, patents fall both upon the just and the unjust and the result is injustice and chaos.

So much has already been written on the general deficiencies of our patent system that it seems futile to join in the chorus, but the situation is so grotesque when applied to the silicate industries that it is our duty to raise our voice in protest.

Such a complaint is the more justified when one considers that the remedy is neither difficult nor complex. The creation of a small committee of experts for each of the natural divisions of industry and technology, among them one for the field of ceramics, would bring about the desired change, namely, full protection of original ideas and rejection of the undeserving claims. By making the experts responsible to the Government in their oath of office, there is every reason to believe that under the guidance of the regular officials the work would be well and efficiently done.

It would be folly to place the blame for the present conditions upon the hard-working examiners of the patent office. It was not intended that they should be omniscient and they are doing the best they can. However, when so many things are being changed for the better these days it is our devout hope that something be done in the matter of our patent system.

PROFESSIONAL DIVISIONS.

It would appear that in the "Professional and Industrial Division" idea, there lie great possibilities for a broader and more useful activity and permanent growth of the American Ceramic Society. Carefully and successfully worked out, it will remove the greatest barrier to growth in membership with which the Society has had to contend in the past, namely: indifference of members, especially the practical man, to regularly attend meetings at considerable expenditure of time and money when 90 per cent of the program is either "high brow stuff" passing way over his head, or else devoted to an industry having nothing akin to his own.

In order to secure the fullest exchange of views on mutual problems, the confrères must feel at ease, which is certainly not the case when the average man gets on his feet to discuss a paper in a regular meeting, with the stenographer interrupting in about the middle of the second sentence to ask his name and the man himself realizing that if he should happen to use the word "about" or "approximately" someone would be sure to pop up the minute he was through and "object to the use of the word 'about' on the floor of this Society, etc." Everyone who has ever attended

the Society meetings knows that time and again points are raised which certain men in the room could and would gladly clear up were it not for a reluctance they feel in rising to their feet under the conditions which usually prevail at our general meetings.

Industrial Divisions will do away with this to a large extent. Members in the same or allied industries will gain the confidence of and learn to know each other better and great good will result. Of course, it is not to be presumed that the general meetings will be entirely superseded by the Division meetings, but rather that a portion of the time will be set aside for the latter purpose. If the Industrial Divisions could continue to hold periodic meetings throughout the year, so much the better, but even if the Division meetings are confined to two each year, at the annual and summer meetings, they will justify their organization.

THE GLASS INDUSTRY.

The desirability of securing the more active coöperation of the glass industry with the American Ceramic Society has been repeatedly emphasized. The rapid progress which has been made in this country during the past four years in the technical advancement of certain branches of this industry should serve to awaken the interest of the other branches in a representative technical organization such as the American Ceramic Society.

The Society has been fortunate in securing a gratifying number of excellent papers on glass for publication in the numbers of the Journal issued thus far and in receiving the assurance of an adequate supply of papers of interest to glass technologists for the future numbers.

Particular attention is called to the fact that the present number includes three excellent papers of both practical and technical value to those engaged in the glass industry. It is to be hoped that our members will bring this number to the attention of their friends and acquaintances who have not as yet become actively interested in the Society.

ORIGINAL PAPERS AND DISCUSSIONS.

THE IDENTIFICATION OF "STONES" IN GLASS.

By N. L. BOWEN.

Introduction.

In glasses intended for a great variety of uses, and particularly those for use in optical instruments, homogeneity is a principal requirement. It is one of the tasks of the glass-maker, therefore, to eliminate foreign particles and inhomogeneity of any kind in such glasses. Foreign particles may be of a gaseous nature, when they are termed seeds, bubbles, blisters, etc. Foreign material may be of a vitreous nature, when it is described as tears, cords, striae, etc., and, finally, foreign particles of a crystalline nature are commonly called stones. Complete elimination of all of these is never attained in glass practice, with the result that selection of the product is usually necessary and the amount of acceptable material becomes a measure of the efficiency of the process of manufacture. In this paper attention is directed towards the occurrence of stones in glass, and particularly towards the information regarding the nature of stones that is to be gained through the use of the petrographic microscope. Since an exact knowledge of the nature of a defect in any material may be a fundamental factor in achieving its elimination, it is hoped that this study of stones in glass may be of some service to the glass-maker. It should be remarked that most of the stones examined by the writer were those encountered while he was engaged in the production of optical glass.

Varieties of Stones.

It has been the experience of glass-makers that a variety of factors may give rise to stones. A classification of stones according to their origin may be given as follows:

1. Pot stones
2. Batch stones
3. Crown drops
4. Devitrification stones

It is often a matter of great importance to a glass-maker, when his glass is running stony, to be able to refer the stones definitely to one of these four classes. If they are pot stones, *i. e.*, actual fragments of the pot, he must look for the trouble in his clays, in his treatment of the pots, in excessive temperature of his furnaces or in a particularly, and perhaps unnecessarily, corrosive glass batch. If they are batch stones, or residual batch material undissolved, he must look to the grinding and mixing of his batch materials, to a proper balance in the proportions of these materials, or to the possibility of too low a temperature at some stage of the melting process. If they are crown drops the grade of bricks used in the crown or the length of flame must be considered. If they are devitrification stones, formed by devitrification or crystallization of the glass after it has been completely melted, he must look to the rate of cooling or to an ill-chosen glass composition.

Identification of Stones.

Chemical analysis of stones is sometimes resorted to in order to determine what their origin may be, but it presents considerable difficulty. Stones are usually quite small so that the chemist must, as a rule, work with a small amount of material; indeed it is sometimes impossible to obtain an adequate amount. It is no easy matter to separate stones from the enclosing glass, so that he must work with contaminated material. As a result of these various factors a chemical examination may consume much time and even then may be unsatisfactory. Then again there are certain types of stones whose chemical composition alone may leave one in some doubt as to the class in which they should be placed. With the aid of the petrographic microscope, on the other hand, it is usually possible to determine rapidly and decisively the origin of a stone, since not only its mineral composition is determinable, but also its internal structure and its relations to the surrounding glass.

The best method of examining stones under the microscope is

to crush them to a powder and examine the powder in a drop of liquid on a slide after covering with a cover slip. With the aid of a set of liquids of various known refractive indices, the high and low indices of the crystals can be measured by the method of comparison and at the same time extinction angles, optic axial angles and other distinctive optical properties observed. The method is highly advantageous for fine materials intimately intergrown, because immersion in a liquid corresponding in index to one of the materials presents the other in marked relief and renders possible a study of the details of the manner of intergrowth.

Pot Stones.

Pot stones are occasionally large enough that when broken open they reveal their nature to the unaided eye. Usually they are quite small, however, and even when formed from pot material that burns very dark they are snow-white and in this respect indistinguishable from stones of different origin. Under the microscope, pot stones are found to be made up, in all cases, of crystals of sillimanite with a little interstitial glass. The sillimanite or aluminium silicate (Al_2SiO_5) is recognized by its usual crystallographic and optical properties identical with those of the natural mineral. Sillimanite is never found in stones of other origin.

It may be remarked in passing that this recrystallizing action of the glass on the pot material is operative not merely on fragments of the pot that have become detached, but also on the wall of the pot itself. The result in this case is the formation of a thin but conspicuous white layer on the inner surface of the pot that is made up of minute crystals of sillimanite with a little interstitial glass.¹ In attacking pot material the glass evidently acts selectively, dissolving first from the clays the portion of the silica in excess of that necessary to form sillimanite. All glasses act alike in this respect so that sillimanite is a universal constituent of pot stones and of the white layer formed on pots whatever may be the composition of the glass. As a result of this selective action of glass on clay material, the more silicious pots are much

¹ G. V. Wilson has examined this white layer and found it to contain crystals of sillimanite. See S. N. Jenkinson, *J. Soc. Glass Tech.*, 2, No. 5, 14 (1918).

more vigorously attacked than the more aluminous varieties. This does not necessarily mean that the silicious pots give more stony glass, however, for the stones formed may be more readily assimilated by the glass. It is rather a lack of uniformity in pot material that is to be avoided, for this may give local pitting and the casting of highly resistant stones.

Having ascertained that stones have their origin in his pots, the glass-maker may then take such steps to remove them as naturally suggest themselves, such as more careful preheating of his pots, altering the glass batch to render it less corrosive, melting at lower temperature, and, of course, altering the pot batch.

Batch Stones.

The only normal constituent of a glass batch that is ever left unassimilated by the glass is the sand. It then occurs as whitish grains embedded in the glass and having the same general appearance as stones of any other type. Under the microscope batch stones are found to consist entirely of silica in one of its forms. Frequently there persists in the grain a core of the original quartz of the sand and this is surrounded by a layer of cristobalite or a mixture of cristobalite and tridymite. Occasionally a small grain may be altered entirely to cristobalite and tridymite, when the core is a dense mass of that material without interstitial glass, differing in this respect from these forms of silica when they occur in devitrification stones to be described later. These various forms of silica are readily recognized by their characteristic optical properties. Excessively fine-grained cristobalite and tridymite are not readily distinguished the one from the other, but this is often a matter of no great moment since the material is readily recognized as one of the low-refracting forms of silica.

A batch stone is usually surrounded by an aura of glass of lower refractive index than the glass as a whole and frequently there is a "tail" of similar material (see Fig. 1). These are the result of the gradual solution of the silica of the stone and are wholly lacking in the case of silica stones that originate through devitrification.

For the elimination of batch stones, the glass-maker should melt at a higher temperature or introduce more "fluxes" into the

batch, that is, he should proceed in a manner directly opposed in most respects to that required for the elimination of pot stones, wherefore the importance of distinguishing these two types of stones. There are, of course, other possible remedies for batch stones, such as the use of finer or more uniform sand, the careful mixing of batch ingredients, etc.



FIG. 1—Batch stones with tails. An extreme example.

Occasionally, through the careless handling of batch materials, they may acquire extraneous matter that is unassimilable by the glass and therefore appears as stones. Identification of such stones may sometimes be accomplished under the microscope and a clue as to source thereby obtained.

Crown Drops.

When the crown of a furnace becomes rather badly corroded by the vapors that are given off by glasses, some liquid may drip from the bricks of the crown and carry particles of the brick with it. Where silica bricks are used, as they commonly are in American practice, grains of silica are thus introduced into the metal and may persist in the finished product. At first thought it would seem that particles of silica added in this manner would differ in no particular from grains left over from the batch, but as a matter

of fact they usually can be distinguished. When quartz is acted on by fluxing materials it changes first to cristobalite, even at temperatures where tridymite is the stable phase, and then the cristobalite is gradually made over into tridymite. For this reason the silica of batch stones, which is fluxed in the glass for a comparatively short period, is predominantly cristobalite and usually very fine grained, for it is continually dissolving and has no opportunity to grow to large dimensions. The silica from the crown, however, has been fluxed for a long period in the liquid that forms on the surface of the bricks before it arrives at that state where drops are likely to form. In the writer's experience of both regenerative and blast furnaces, complete conversion to tridymite is accomplished in this surface material and rather large crystals have grown that are easily distinguished from the fine-grained cristobalite of batch stones. From furnaces whose crowns are maintained at temperatures above 1470°C for lengthy periods, which is rarely done in glass practice, cristobalite should be formed rather than tridymite, and Merwin describes cristobalite from the crown of a recuperative furnace.¹ In such a case the rule that crown drops are made up of tridymite would not hold, but even here it seems likely that the cristobalite would have grown to much larger dimensions than in batch stones and might be distinguished by this fact. Of course one can always determine, for any particular furnace, the exact nature of the material that would enter into the formation of crown drops by chipping off some of the glaze from the bricks of the crown when it is cold enough to render this possible.

Devitrification Stones.

Devitrification or crystallization of glass may make its appearance in various forms. When crystals are formed that are large enough to be seen as individuals with the unaided eye and are disseminated through a glass which is otherwise clear and transparent, they are usually described simply as crystals and the glass is said to have undergone "crystallization." When the crystals are small and closely spaced, so that the effect is to render

¹ Ferguson and Merwin, "The Melting Points of Cristobalite and Tridymite," *Am. J. Sci.*, [4] 16, 424 (1918).

the glass an opaque white mass, the glass is said to have undergone "devitrification." There is, however, no essential difference and such difference as appears is simply the result of the limitations of the human eye. Under the microscope a piece of "devitrified" glass is seen to consist of a clear transparent glass base through which crystals are dotted, the whole appearance being the same as that presented to the unaided eye by a piece of glass that has undergone "crystallization," as that term is used above. While the formation of minute crystals in glass, in such manner that the whole mass is rendered opaque, can hardly be referred to as the formation of stones, it is, however, considered to some extent here since the phenomena are fundamentally the same. A common misconception concerning devitrification should, perhaps, be mentioned at this point. It is sometimes considered, when a piece of glass is rendered a dense opaque mass, that it has crystallized as a whole. This is far from the truth. Almost invariably there are formed crystals of only one of the compounds occurring in the glass and the crystals themselves seldom amount to more than 10 or 15 per cent of the total mass of glass.

A common form of crystallization or devitrification is that in which spheroidal masses of crystalline material are formed in the glass. These are analogous to the spherulites that occur in natural glasses, *i. e.*, volcanic lavas. In artificial glasses they are made up of innumerable minute crystals of one of the constituents of the glass radiating from a center and having glass in the interstices between the crystals or radii. These spherulites constitute the typical devitrification stones. Occasionally crystallization of this kind begins with the formation of a rather large individual crystal and is continued, as the glass becomes more viscous, by the growth of a spherulite about this crystal.

Silica, the fundamental constituent of nearly all glasses, is perhaps the commonest ingredient that separates from them. It may separate as minute crystals, evenly disseminated, when it gives an opalescent, milky or a dense opaque glass according to the size of the crystals. Under exceptional conditions large individual crystals of tridymite have been noted.¹ Finally it may

¹ H. Le Chatelier, *Bull. Soc. Min. Fr.*, 39, 150 (1916).

separate in the form of spherulites which have special interest in this connection since they constitute typical stones.

The silica contained in spherulites of this type is, in the writer's experience, principally in the tridymite form though some cristobalite is usually present and occasionally may predominate. Though a spherulite may appear to be entirely crystalline it is really composed principally of glass with a relatively small proportion of crystals, the glass being interstitial between the radiating crystal fibres. While frequently of the same mineral constitution, these spherulites are unlike batch stones in that there is no central core of a dense crystalline nature free from glass, and there is, of course, never a core of quartz. The interstitial glass of tridymite spherulites is appreciably higher in refractive index than the main mass of glass surrounding the spherulite because there is an abstraction of silica from the interstitial glass. The glass surrounding a spherulite is, however, not appreciably affected by this action. A spherulite grows entirely, then, at the expense of the glass contained within it. It is for this reason that chemical analysis of a spherulite shows it to have sensibly the same composition as the main mass of glass, a fact which has sometimes led to the erroneous conclusion mentioned above, that the glass as a whole mass has crystallized.

The compound CaSiO_3 separates rather frequently from glass. This compound is known in two crystalline modifications, wollastonite, stable at temperatures below 1170°C , and pseudowollastonite, stable at higher temperatures. According to Le Chatelier, pseudowollastonite forms in some glasses,¹ but the writer has seen only wollastonite. In one example seen by the writer, fairly large individual crystals up to 3 mm. in length were found in plate glass. Usually, however, the wollastonite forms typical spherulites. Some spherulites of this type found in a window glass tank (see Fig. 2) and examined by the writer, show radiating prismatic fibres of wollastonite with some interstitial glass that is thickly dotted with minute crystals of cristobalite. Wollastonite crystals as found in glass have properties identical with those of the natural mineral and given on a later page.

Besides wollastonite, which may separate from ordinary lime-

¹ *Bull. Soc. Min. Fr.*, 39, 150 (1916).

soda glasses, and silica, which may separate not only from these but also from many special glasses, there are certain compounds that separate only from special glasses.

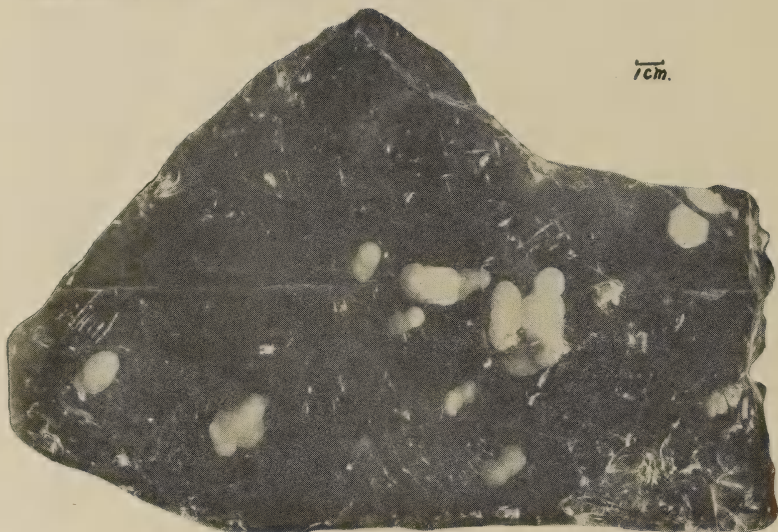


FIG. 2.—Spherulites of Wollastonite (CaSiO_3) in Glass.

From some barium crown glasses the compound BaSi_2O_5 may separate.¹ It may form fairly large individual crystals (see Fig. 3) if crystallization begins at a high temperature, and about these crystals spherulitic growth may take place as the temperature falls. If crystallization takes place entirely at the lower temperature a simple spherulite may form. Such spherulites or stones are readily distinguishable from other stones by the characteristic properties of BaSi_2O_5 .

From glasses very rich in lead, spherulites sometimes separate, the fibres of which appear to agree in general properties with the natural mineral alamosite, PbSiO_3 .

All spherulites have the same radiating fibrous structure that is described in connection with silica spherulites.

All of these types of devitrification stones are readily recognized

¹ N. L. Bowen, "Crystals of Barium Disilicate in Optical Glass," *J. Wash. Acad. Sci.*, 8, 265 (1918).

as such by the characters that have been mentioned here in connection with them. The ability to recognize them may, in itself, be an important aid to the glass-maker, but the ability to determine the exact composition of the crystals that separate may be a still more important factor. The separation of a certain compound frequently indicates an excess of that compound in the glass and may point to mistakes made in the batch room or to variability in the composition of one of the raw materials. The nature of the compound separating suggests which one of the raw materials should be suspected. If these factors have

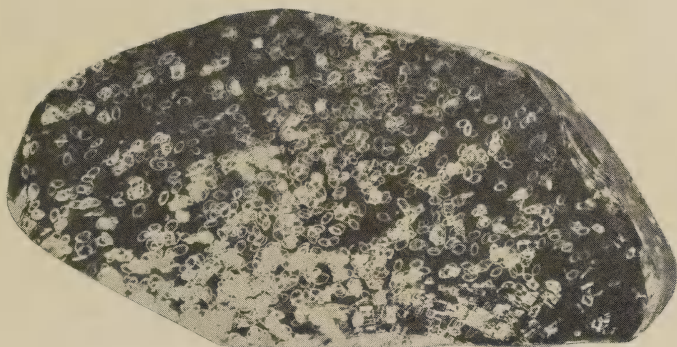


FIG. 3.—Crystals of BaSi_2O_5 in Glass. (Natural size).

been checked and found satisfactory, then the difficulty must be sought in an ill-chosen batch composition. Nearly always some readjustment in the chemical composition of a glass can be made without making a change of properties too great to spoil the glass for its particular use and the nature of the crystals that separate furnishes a clue to the direction in which this change of composition should be made. When a change of composition is not permissible, the glass-maker must endeavor to vary his heat treatment in such a way as to reduce the formation of the devitrification stones to a minimum.

Optical Properties of Crystals Occurring in Glass.

The following is not intended to be a complete statement of the optical properties of the crystals described. It gives merely those

properties that are of greatest use in distinguishing the crystals as they are found in the glass.

Sillimanite (Al_2SiO_5) is orthorhombic and occurs in glass in lath-shaped crystals with parallel extinction and positive elongation. The refractive indices are $\gamma = 1.681$ and $\alpha = 1.660$ and can be measured even on very small crystals embedded in glass, for by careful search of the powder immersed in liquid one can always find crystals that have not been broken across and therefore present an edge against the liquid. The refraction is higher than that of all glasses except the very heavy lead glasses, which fact enables one to distinguish even excessively minute crystals from those of cristobalite or tridymite. The double refraction, $\gamma - \alpha = 0.021$, is moderately strong.

Silica may occur in glass in any of the three forms *quartz*, *tridymite* or *cristobalite*.

Quartz occurs only rarely and then as sand that has remained unaltered. It is uniaxial and positive; $\epsilon = 1.553$ and $\omega = 1.544$.

Tridymite occurs as thin hexagonoid plates that appear as needles when turned on edge and have parallel extinction and negative elongation. They frequently show the characteristic parallel growth of overlapping plates. The refractive indices are $1.469 - 1.473$, the refraction and double refraction being therefore both very low.

Cristobalite frequently occurs as skeleton crystals consisting of minute octahedra arranged in parallel growth on a cubic pattern and having a general similarity to magnetite, native gold or other cubic minerals when they form skeleton crystals. When free to grow larger it may form elongated cubes that are, however, never sufficiently elongated to be confused with "needles" of tridymite. The cubes are sometimes terminated by octahedra that have somewhat greater dimensions than the cube and give club-shaped or spear-shaped crystals. The refractive indices are $1.484 - 1.487$, somewhat higher than those of tridymite. Probably as a result of the compensating effect of intricate twinning, cristobalite usually appears to be nearly isotropic.

Barium disilicate (BaSi_2O_6), is orthorhombic and occurs as thin six-sided plates (see Fig. 3) with parallel extinction and negative

elongation. The refractive indices are $\gamma = 1.617$ and $\alpha = 1.598$.¹ In connection with the sign of the elongation it should be noted that a lath-shaped section representing a plate broken across may be either positive or negative.

Wollastonite (CaSiO_3), though monoclinic, appears in glass as crystalline needles or laths with parallel extinction, because elongated parallel to b , the axis of symmetry. The elongation is either positive or negative, depending on the plane in which the lath is turned. The refractive indices are $\gamma = 1.633$ and $\alpha = 1.620$.

Summary.

The petrographic microscope is a convenient and efficient instrument for the determination of the nature and origin of "stones" or crystalline particles occurring in glass. Stones are divided into four classes: (1) *pot stones*, (2) *batch stones*, (3) *crown drops*, (4) *devitrification stones*. These classes have distinctive features of structure and texture that are revealed by the microscope. Moreover, the crystalline phases contained in stones can be identified by a determination of their optical properties. The results of a study of stones by these methods are given in this paper.

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CARNEGIE INSTITUTION OF WASHINGTON,
WASHINGTON, D. C., December, 1918.

¹ For a more complete description of barium disilicate see N. L. Bowen, *J. Wash. Acad. Sci.*, 8, 265 (1918).

SOME TYPES OF PORCELAIN.¹

By F. H. RIDDLE AND W. W. McDANIEL, Pittsburgh, Pa.

Introduction.

The present work deals with porcelain bodies burned at temperatures equivalent to the softening point of cone 10 or above. This includes the firing range of electrical porcelain and of most hotel china as well as of wares fired to higher temperatures—such as chemical porcelain and some of the imported chinas. Some table porcelain made in the United States is burned to cone 13 or 14 but the production is very small. Some of the French, Austrian and other imported wares are burned at from cone 15 to 18.

The European practice is to bisque the ware at a low temperature and to carry the glaze temperature to the maturing point of the body. This, of course, necessitates the use of a glaze maturing at the same temperature as the body. The glaze and body are thus brought into very intimate contact, since the glaze, as it softens, is absorbed by the porous body before the latter closes up and becomes impervious. This penetration of the glaze is merely along the surface but is sufficient to produce a strong bond between the body and glaze.

The American practice is to mature the body in the bisque burn and to use a glaze which matures at a lower temperature. For example, we may bisque to cone 11 and glaze to cone 4 or 5. This method has many manufacturing advantages. It is not, however, the purpose of this paper to discuss the relative merits of the two processes.

The Field Covered.

The chief purpose of this study was to determine the burning range of porcelain bodies having compositions covering the ordinary porcelain field fired at cone 10 and above. In Table 1 are given the compositions of the bodies used. It will be noted that the clay content varies from 45 to 85 per cent and that the

¹ By permission of the Director, Bureau of Standards.

TABLE I.¹
COMPOSITIONS USED.

Body number.	Clay content. Per cent.	Feldspar content. Per cent.	Whiting content. Per cent.	Flint content. Per cent.
16 to 23	45	16-30	...	39-25
24 to 31	50	16-30	...	34-20
32 to 39	55	14.5-28.5	1.5	29-15
40 to 47	60	14.5-28.5	1.5	24-10
51 to 55	70	10-28.5	1.5	18.5-0
56 to 59	75	10-23.5	1.5	13.5-0
60 to 62	80	10-18.5	1.5	8.5-9
63	85	13.5	1.5	0

flux content varies from 10 to 30 per cent. In several of the bodies of high clay content the flux content has necessarily been

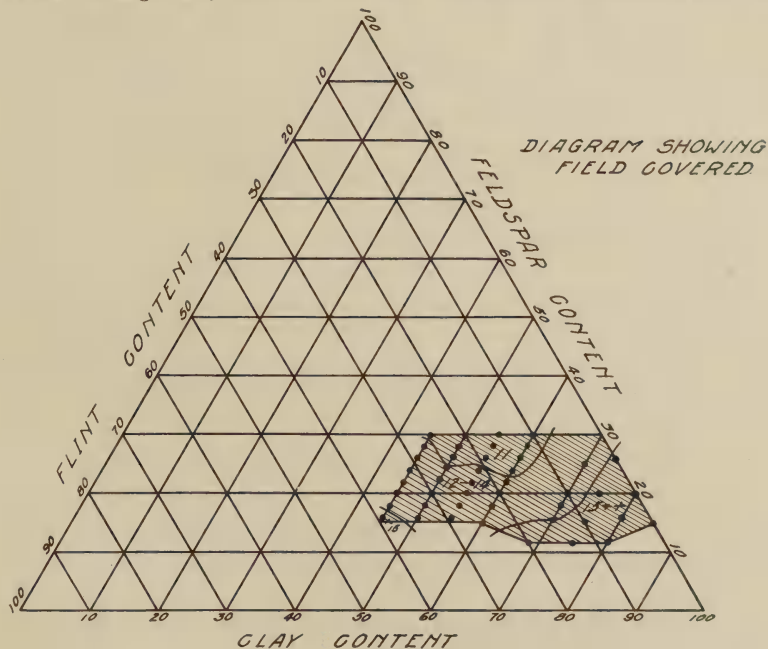


FIG. 1.

¹ The clay content was made up of equal parts of Georgia, Florida, North Carolina and Delaware kaolins. Where the clay content was over 55 per cent the balance was calcined to cone 14 and ground dry to pass a 120 mesh sieve.

reduced. No ball clay was used in any of the bodies of the first series, the clay content having been derived from equal parts of four American clays, namely, North Carolina, Florida, Georgia and Delaware kaolins. In all cases in which the clay content was more than 55 per cent, the balance was calcined. It would not, of course, be a common practice in the manufacture of ware, excepting in a few cases, to entirely eliminate ball clay. The effect of ball clay is shown later. It is a fact that most of the vitreous pottery bodies made in this country at the present time contain but small amounts of ball clay. In the triaxial diagram (Fig. 1) is shown the field covered.

Methods of Testing.

The method of procedure in testing the different bodies was that ordinarily used in work of this kind. The bodies were weighed out from standard grade materials—previously dried so that no allowance was necessary for moisture. Two five-kilogram charges of each body were weighed out and ground wet for three hours in a ten-inch ball mill. Throughout the work all conditions of testing were maintained as nearly constant as possible. After grinding, the two bodies were mixed, passed through a 140-mesh silk lawn, and filter-pressed. The filter cakes were then thoroughly hand-wedged and made into ware. Unless otherwise noted, the material was made up into ware three days after having been filter-pressed. The only bodies that were prepared under different conditions were those made with varying times of grinding and with varying times of ageing. The bodies were molded principally into draw trial pieces and standard cups for the determination of the dielectric resistance. In certain cases moduli of rupture bars, crushing cubes, and pieces of chemical- and table-ware were made, this depending upon the character of the body.

The tests on each body included the determination of the water of plasticity, the drying shrinkage (by volume), the apparent specific gravity in the dried state, and the porosity and volume changes at different firing temperatures. In some cases additional tests such as the transverse, crushing, etc., were made.

Water of Plasticity.

The previously prepared clay, in the proper working condition, was forced from a hydraulic-plunger press through a die $1\frac{1}{8}$ " square (with slightly rounded corners). The bars were cut into test pieces $1\frac{1}{2}$ inches long. For the determination of the water of plasticity, three of the pieces were weighed immediately after being made and again after having been thoroughly dried at 110°C .

Drying Shrinkage.

In making this determination the wet briquettes were immersed in kerosene immediately after molding and weighing. The volumes were then determined in a voluminometer of the Seger type, provided with a burette reading to 0.05 cc. After removing the specimens, they were dried, first at atmospheric temperatures and finally at 110°C . The dry specimens were weighed at once, again immersed in kerosene (usually for twelve hours) and the volumes were then determined as before. The shrinkage was computed in terms of the dry volume. From the weights of the dry specimens and their volumes, the apparent specific gravities were computed.

From the wet and dry weights and the wet and dry volumes of the briquettes and the true specific gravity of the clay, it was possible to calculate the volume of the shrinkage and the pore water in terms of the true clay volume. These computations were based on the following relations:

$$\frac{100 S (W_1 - W_2)}{W_2} = a = \left\{ \begin{array}{l} \text{volume of shrinkage water, in terms} \\ \text{of the true clay substance, ex-} \\ \text{pressed in per cent.} \end{array} \right.$$

$$\frac{100 S (V_1 - V_2)}{V_2} = b = \left\{ \begin{array}{l} \text{volume of shrinkage water, in terms} \\ \text{of the true clay substance, expressed} \\ \text{in per cent.} \end{array} \right.$$

In these formulas:

S = Specific gravity of body (approaching the value of 2.6 quite closely)

W_1 = weight of briquette in the wet state

W_2 = weight of briquette in the dry state

V_1 = volume of briquette in the wet state

V_2 = volume of briquette in the dry state

The value $a - b$ represents, similarly, the volume of pore water and the ratio $\frac{a - b}{a}$, the relation of pore to shrinkage water.

By dividing b by a , and multiplying by 100, the percentage of shrinkage in terms of the volume of total water may be computed.

Modulus of Rupture.

Test pieces in the form of bars $7'' \times 1'' \times 1''$ were carefully molded from a thoroughly wedged piece of clay by wire cutting to as near the mold size as possible and then carefully placing in the mold in one piece, pressing in, and trimming off with a wire at the top. The properly numbered pieces were dried at room temperature, heated at 110°C , cooled in a desiccator, and immediately broken transversely. In all cases ten pieces were broken and the average result taken.

Burning Behavior of the Clays.

The draw trial briquettes, after having had their dry volumes determined, were placed in a test kiln, fired with natural gas and compressed air, and burned at a rate corresponding to a temperature increase of 20°C per hour above 800°C . Beginning at 1200°C , the briquettes were drawn from the kiln at intervals of 30°C . This was continued up to 1440°C and, in case the bodies were extremely refractory, the temperatures were carried higher until the pieces became overburned. All pieces, as they were drawn from the muffle, were placed as rapidly as possible in an annealing furnace and cooled down gradually in order to prevent shattering. When cool, the briquettes were weighed, immersed in water, boiled in a partial vacuum for five hours, again weighed suspended in water, and finally weighed in air when fully saturated with water.

From these data, the porosity was calculated by the use of the Purdy formula.¹ The volumes of the briquettes were determined by means of the voluminometer—kerosene being used as the displacing liquid. The volume shrinkage or expansion was invariably expressed in terms of the original volume in the dried state. Both the porosity-temperature and the volume-temperature rela-

¹ R. C. Purdy, Ill. Geol. Surv., *Bull.* 9.

tions are extremely significant in the study of the burning range and behavior of a body. When plotted, the information presents an easy method of study and comparison. Zero porosity, or better, zero absorption, may be considered the first point of maturity. A more sensitive criterion of maturity is the point of greatest density or smallest volume and it should correspond to the most suitable temperature for burning the ware. As soon as overburning—due to the formation of a vesicular structure—starts, the volume increases and a drop in the curve is noted. It is evident, then, that the greater the difference in temperature between the point at which zero porosity is first reached and that at which overburning is evident, the wider is the firing range of a body. When the overburning advances far enough, there will be an increase in porosity—due to water entering some of the outside pores that have been ruptured. The volume change will, therefore, indicate overfiring earlier than the porosity relation.

Considerable care and accuracy is necessary in making draw trial burns in order to make comparison possible between several burns. Thus far, seven burns have been made in the work under discussion. The kiln was large enough to hold all of the briquettes for seventeen bodies. As a check against the thermo-couple and pyrometric cones, it has been our practice to burn a set of draw trials of the same body in several burns and to check the results by comparison.

The Effect of Increasing the Feldspar Content and Maintaining the Clay Content Constant.

This is very well illustrated in Fig. 2. The bodies used were Numbers 17, 19, 21 and 23 of Table 1, their compositions together with their burning ranges being given in Table 2.

TABLE 2.

No.	Composition.			Temp. of zero absorption.	Temp. of maximum density.	Temp. of start of overburning.
	Per cent clay content.	Per cent feldspar content.	Per cent flint content.			
17	45	18	37	1380° C	1410° C	1440° C+
19	45	22	33	1350° C	1380° C	1410° C+
21	45	26	29	1320° C	1350° C	1410° C—
23	45	30	25	1320° C	1350° C	1380° C

A study of the results shows that the range is not much wider for the low feldspar than for the high feldspar bodies—though there is some difference. This is better shown by the curves than by the numerical values. The curves also indicate

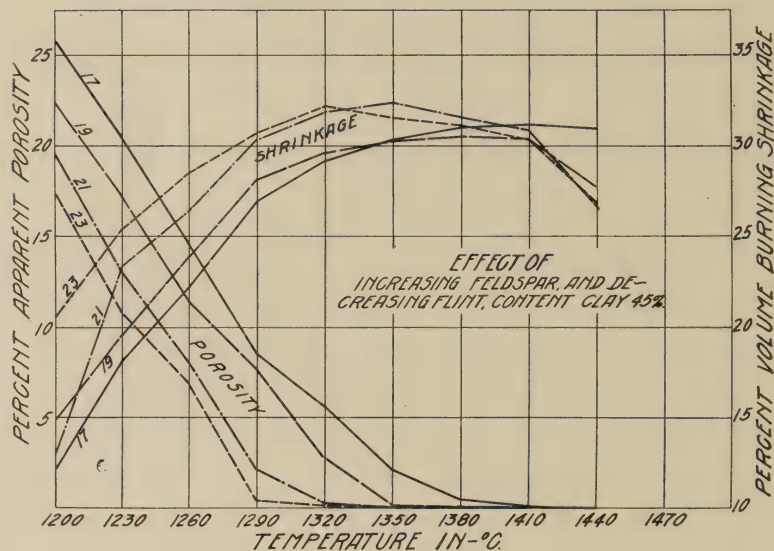


FIG. 2.

that the bodies of high feldspar content appear to approach zero absorption more abruptly. Although the firing ranges of the several bodies are nearly the same, the temperatures of maturity are much lower in the case of the high feldspar bodies—as would naturally be expected.

This same type of curve applies to bodies having a much higher content of clay—up to 75 per cent. In Fig. 3 it will be noted that bodies Nos. 52 and 55 contain 70 per cent clay and that body No. 52 contains $16\frac{1}{2}$ per cent flux and body No. 55 contains 30 per cent flux.

The chief difference in the two sets of bodies, as shown by Figs. 2 and 3, is that the variation in the content of flux has a more marked effect on the low clay (Fig. 2) than on the high clay bodies (Fig. 3). This would indicate, therefore, that the higher

the clay content, the less the effect of variations in the amount of flux. The difference, however, is not great. In fact, it is rather surprising how little difference there is in the burning

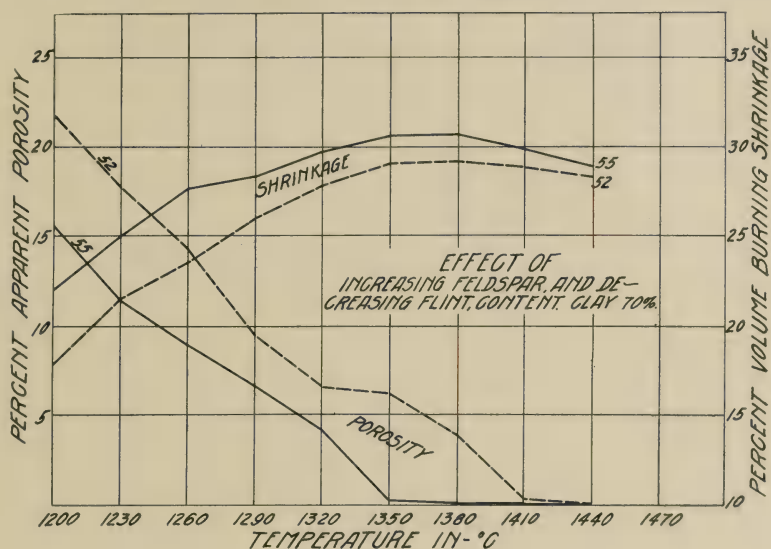


FIG. 3.

ranges of bodies having varying clay contents, so long as the amount of flux used is constant, the flint content decreasing, of course, as the clay content increases.

In Fig. 4 is shown the burning curves for the three bodies, the compositions of which are given in Table 3.

TABLE 3.

Body No.	Per cent raw clay.	Per cent calcined clay.	Per cent feldspar.	Per cent whiting.	Per cent flint.
35	55	..	20.5	1.5	23.0
43	55	5	20.5	1.5	18.0
53	50	20	19.0	1.5	9.5

As noted, these bodies contain 55 per cent, 60 per cent and 70 per cent of clay, respectively. The burning curves for Nos. 35 and 43 are very much alike. Body No. 53 contains less fluxing

material and hence has a somewhat smaller shrinkage but otherwise it is similar to the others.

Referring again to Fig. 2, the burning curves for body No. 19, containing 45 per cent clay and 22 per cent feldspar, is also similar to that of these bodies.

It is interesting to note the similarity in the curves for the bodies represented in Fig. 4, which have variations in clay content

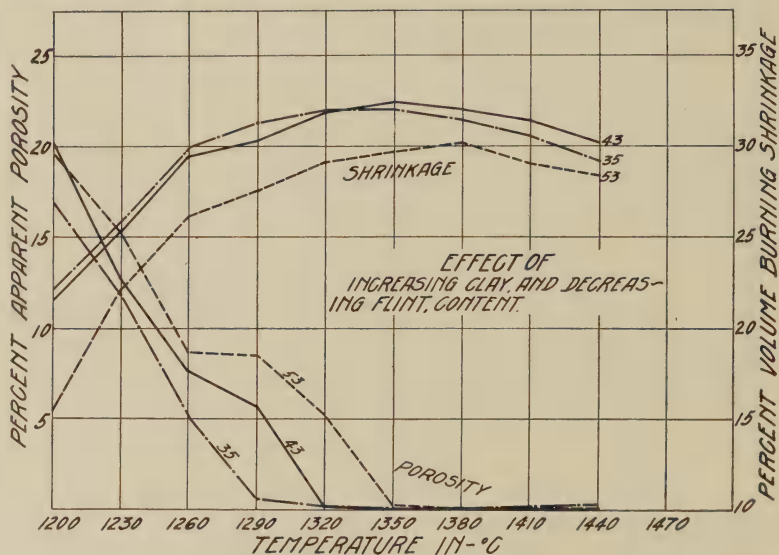


FIG. 4.

from 55 to 70 per cent but the same content of flux, to the bodies shown in Fig 2, which have the same clay content but a wide variation in the flux content. Although body No. 53 does not have exactly the same content of flux as Nos. 35 and 43, it is sufficiently close for comparison and it will be noted that it is a little more refractory than bodies Nos. 35 and 43.

Fig. 5 is an enlarged sketch of the field covered, as shown in Fig. 1, and shows the maturing points of the bodies in the different areas.

It will be noted that the bodies containing 45 and 50 per cent clay vitrify at a slightly higher temperature than those contain-

ing 55 and 60 per cent clay. This, however, is due to the presence of $1\frac{1}{2}$ per cent whiting in the bodies containing 55 per cent and more of clay. The effect of the whiting is shown later.

In this connection, it is of interest to note the softening points of mixtures of Zettlitz kaolin, quartz and feldspar as determined

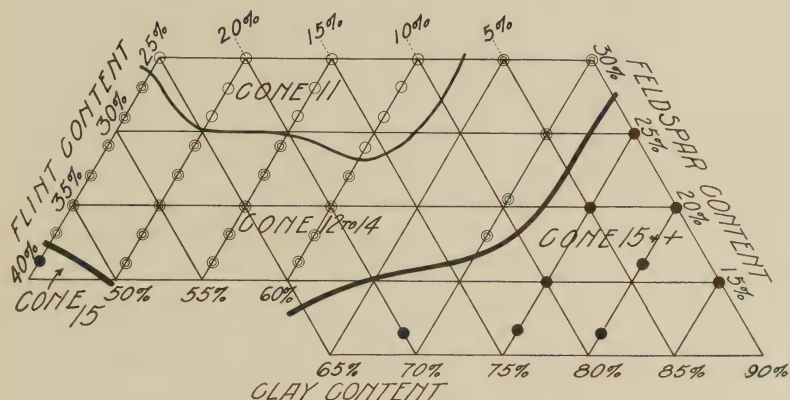


DIAGRAM SHOWING MATURING POINTS
OF DIFFERENT MIXTURES.

FIG. 5.

by M. Simonis.¹ These have been plotted on the triaxial diagram, Fig. 6. The field covered in Fig. 5 is shown in the shaded area of Fig. 6. There is very little variation in the softening points between 45 and 70 per cent kaolin with feldspar variations from $12\frac{1}{2}$ to 30 per cent. There is also more variation between $12\frac{1}{2}$ per cent and 30 per cent feldspar with 45 per cent clay than with 70 per cent clay.

The Effect of Ball Clay.

As previously stated, ball clay was not used in any of the bodies prepared in the foregoing work. On account of its general use and its bonding strength in the green state, tests were made in order to show its effect both in the green state and in the burning. In Table 4 is shown the composition of several bodies, their moduli of rupture, water of plasticity contents, etc. The first four

¹ *Sprechaal*, 1907, No. 40.

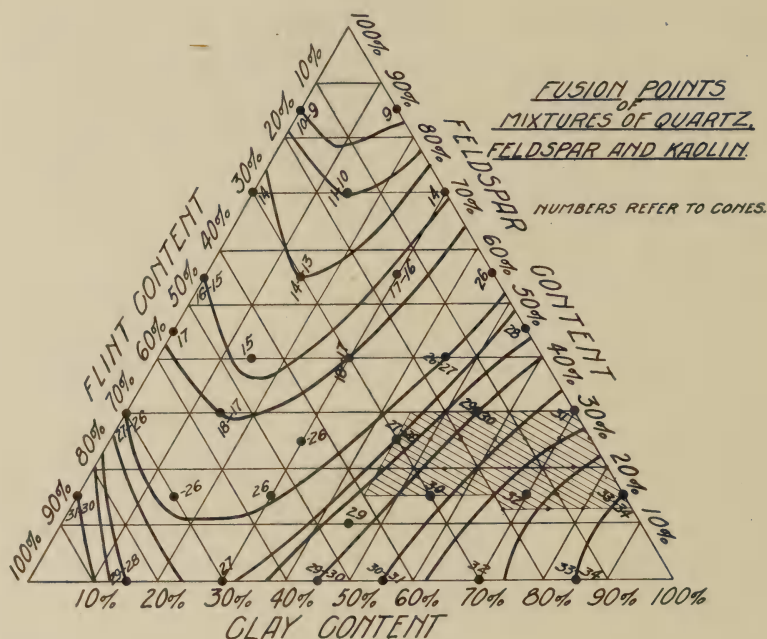


FIG. 6.

are all-kaolin bodies and the remainder of the series contain from 0 to 16 per cent of Tennessee ball clay. Of the first four, two

TABLE 4.

Showing the effect of ageing of bodies containing no ball clay as compared to green bodies containing ball clay.

Body No.	Time aged.	Drying (shrinkage by volume).	Per cent water in terms of dry wt.	Modulus of rupture, lbs. per sq. in.	Per cent ball clay.	Per cent total clay.	Per cent feldspar.
26 old	8 months	19.54	28.12	267.6	0	50	20.0
26 new	3 days	13.98	27.80	139.8	0	50	20.0
34 old ¹	8 months	22.67	31.23	278.8	0	55	18.5
34 new ¹	3 days	14.75	28.70	165.0	0	55	18.5
139 new	3 days	10.25	25.81	157.0	0	45	20.0
140	3 days	11.99	26.44	186.0	4.0	45	20.0
141	3 days	12.07	25.92	201.5	8.0	45	20.0
142	3 days	13.60	26.24	202.0	12.0	45	20.0
143	3 days	14.02	26.32	250.0	16.0	45	20.0

¹ Bodies Nos. 34, old and new, contain 1½ per cent of whiting.

were molded into test pieces three days after preparation and duplicates of these were also molded into test pieces after ageing for eight months—having been kept in a damp closet and in workable condition for the entire time. None of the other bodies were aged.

In both cases when the body was aged the all-kaolin bodies showed a marked increase in strength with age. Ageing increased the modulus of rupture of body No. 26 from 139.8 pounds to 267.6 pounds per sq. in. and of body No. 34 from 165 to 278.8 pounds per square inch. In both cases the aged kaolin bodies were stronger than body No. 143, containing 16 per cent ball clay, the modulus of rupture of this body being 250 pounds per sq. in. It may be of interest to compare the strength of these bodies with the strength of commercial bodies. Several commercial china bodies were tested and their moduli of rupture were found to vary from 170 pounds to 220 pounds per square inch. Several attempts were made to model difficult shapes from the un-aged kaolin bodies. Comparing this with the modeling with the aged kaolin bodies the difference was remarkable.

This is not a proof that ageing will improve the working properties of all bodies, but in view of the fact that it is desirable to make ware as white as possible, it is well to reduce the ball clay content of bodies to as low a figure as possible. If ageing will make this possible it is well worth doing. Several potters, who grind their pottery bodies exceedingly fine, claim that they become unworkable if aged and that the clay at the bottoms of the piles becomes "rubbery," as does clay that contains an excess of alkaline salts. This is quite possible as the fine grinding may reduce the particles of feldspar to such an extent that a part of the salts will become soluble in time and act as casting salts do. If this is true, it then becomes a case of sacrificing one quality for the other and of depending entirely upon what the potter considers the best thing to do. On the other hand, it may be possible to neutralize the alkaline salts by the addition of acid before grinding.

The effects of increasing the ball clay content and the length of time of ageing of bodies are well marked in the burning. In Fig. 7 is shown the volume shrinkage and porosity curves for bodies Nos. 139 to 143, inclusive. The curves show the very

marked effect the ball clay has on the tendency of the body to overburn as well as how increase of ball clay tends to close the body up at lower temperatures—as shown by the porosity curves. Bearing in mind that body No. 139 has about the same composition as body No. 17, it might be well to compare the curves of Figs. 2 and 7. The two sets of curves have quite different characteristics. In Fig. 2 is shown the effect of increasing amounts of feldspar. The increase not only causes the body to overburn at

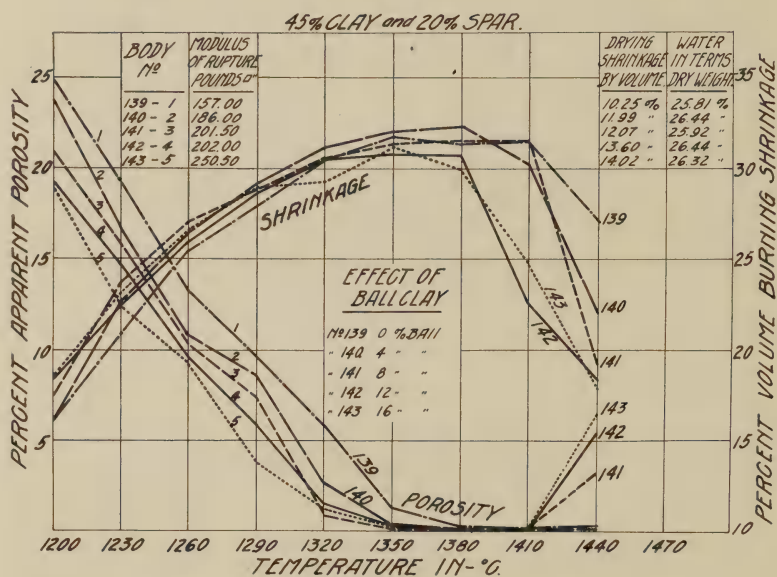


FIG. 7.

a lower temperature but causes it to mature at a lower temperature—the firing range remaining about the same. However, the addition of ball clay, although it matures the body at a lower temperature (compare porosity curves, Fig. 7), also causes it to overburn much earlier in proportion. Up to a certain point, the addition of ball clay will permit of the reduction of the feldspar content.

When these results are compared with those shown in Figs. 8 and 9, the effect of ageing upon the burning behavior of bodies

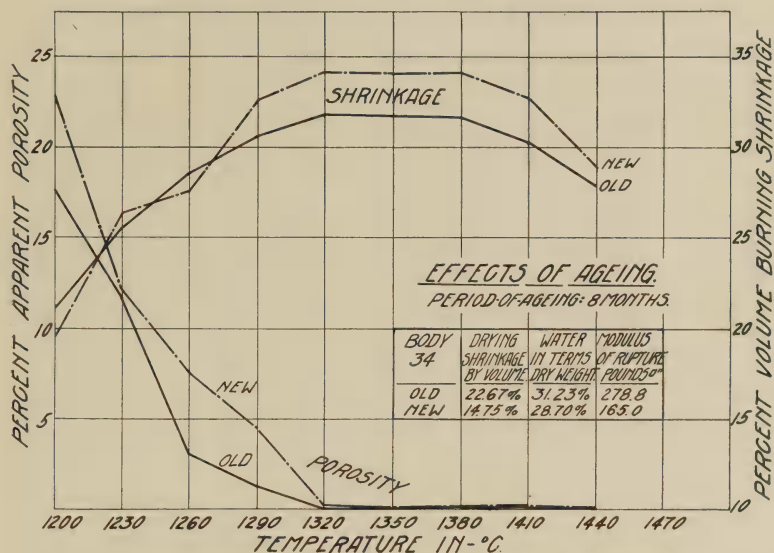


FIG. 8.

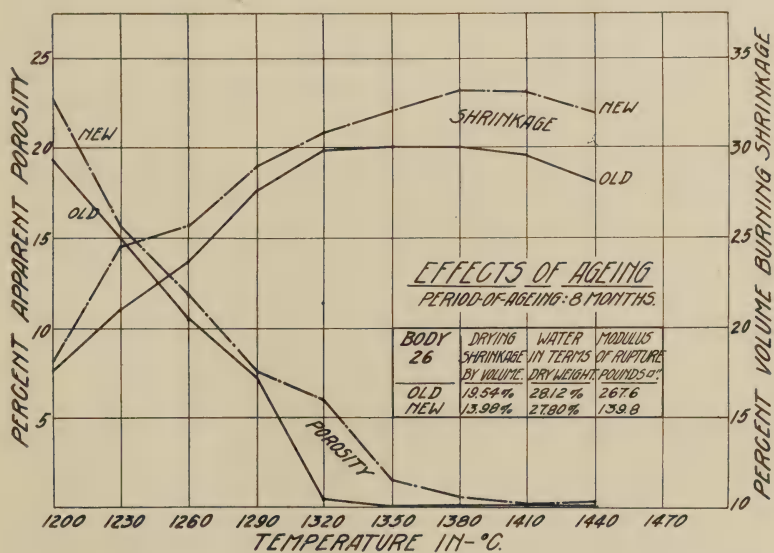


FIG. 9.

Nos. 26 and 34 is apparent. The aged bodies close up somewhat earlier and their shrinkage is less. The curves would also indicate that the ware burns much more uniformly. It has been seen that the difference in the transverse strength of the fresh and aged bodies is greater than that of the body containing zero and that containing 16 per cent ball clay. At the same time the burning range of the fresh and aged bodies is, if anything, in favor of the aged or tough body. On the other hand, in the case of ball clay bodies, the increase of ball clay has a marked effect in the shortening of the firing range. This, then, is still another point in favor of the use of bodies having a minimum content of ball clay but which are improved by ageing. All of the above observations, especially that the aged bodies shrink less than the fresh ones, show that the ageing has a profound influence upon the colloidal portion of the body. If ball clay must be used, as little as possible should be employed.

The Effect of the Addition of Small Amounts of Magnesium, Calcium and Barium Carbonates.

Four sets of bodies were made up with the following body as a base:

6 per cent ball clay
39 per cent kaolin
18 per cent feldspar
37 per cent flint

This body was selected as it contains about as little ball clay as is ordinarily used commercially and a fairly low content of feldspar. Small amounts of flux were introduced for the purpose of securing bodies having lower maturing temperatures. In each case the feldspar was replaced by equal amounts of another flux. The amounts added are given in Table 5.

TABLE 5.

Series 1.		Series 2.		Series 3.		Series 4.	
Body No.	Per cent flux.	Body No.	Per cent flux.	Body No.	Per cent flux.	Body No.	Per cent flux.
164	0.2 MgO	168	0.2 CaO	172	0.2 MgOCaO	176	0.2 BaO
165	0.4 "	169	0.4 "	173	0.4 "	177	0.4 "
166	0.7 "	170	0.7 "	174	0.7 "	178	0.7 "
167	1.0 "	171	1.0 "	175	1.0 "	179	1.0 "

The alkaline earths were introduced as the carbonates. In the third series, equal equivalents of CaO and MgO were added as carbonates.

The curves of Figs. 10, 11 and 12 show very well the effect of the fluxes upon the burning range. The curves for bodies Nos. 172 to 175 are not shown as they are similar to those of bodies Nos. 164 to 167. The principal points to be noted are that BaO shows no noticeable action other than a slight tightening of the body while CaO and MgO produce a very decided effect,

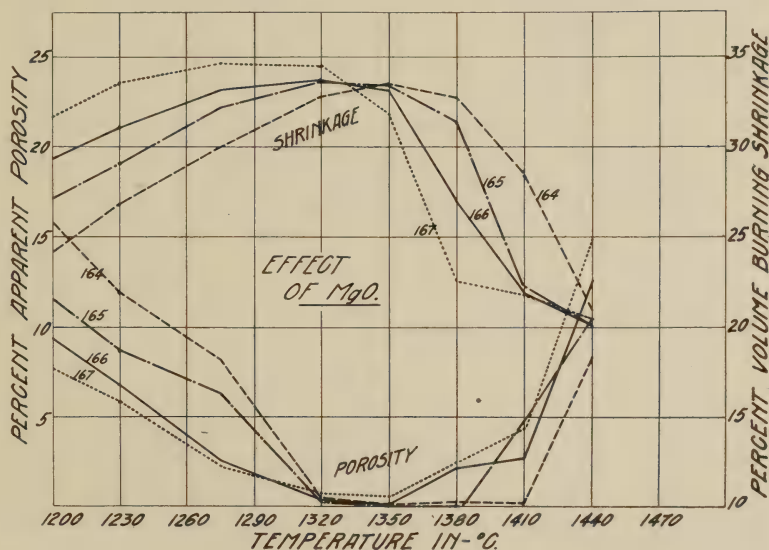


FIG. 10.

the MgO, however, being the more active. It is also very noticeable that the CaO does not hasten the maturing of the body but causes overburning at a lower temperature. Its presence also shortens the firing range considerably. On the other hand, MgO causes the body to mature much earlier and brings about the overfired state at a lower temperature—the former effect being the more prominent. The mixture of the two oxides behaves almost exactly like MgO by itself.

These facts would point to the conclusion that the addition of

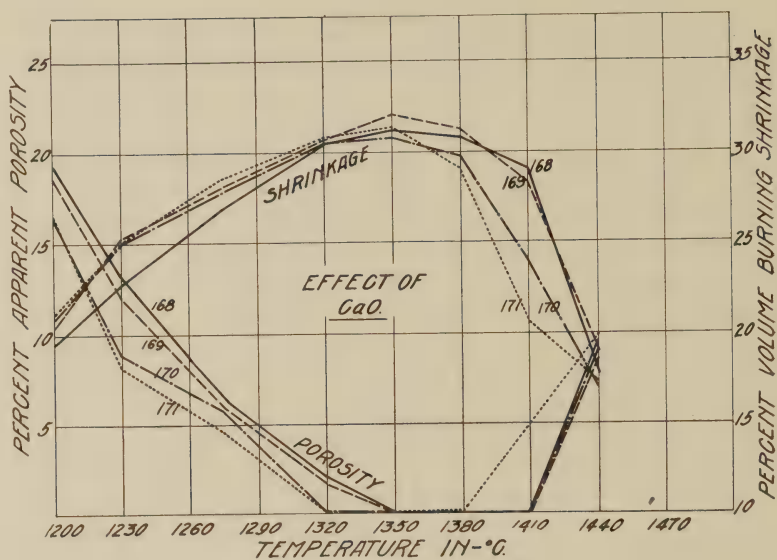


FIG. 11.

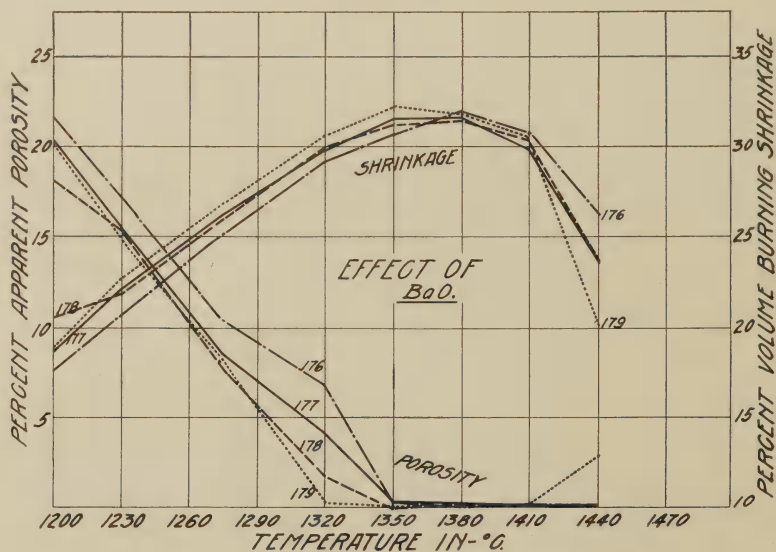


FIG. 12.

a small quantity of magnesite or dolomite would be very beneficial but that the addition of whiting would tend to hasten overburning even though it would assist vitrification of the body. BaO seems to render no useful service. It is also noted that volume shrinkage is greater with the addition of the MgO and MgOCaO than with the addition of CaO or BaO. Those bodies from No. 164 to 179 were made up into ware by several methods.

The body containing no flux, beyond the 18 per cent feldspar, showed no translucency when fired at cone 11, while the bodies to which were added the alkaline earths (with the exception of the barium carbonate) evidenced very marked translucency increasing with the amount added, although there was not a great difference between the effects of the 0.7 per cent and 1.0 per cent additions. The BaO produces no translucency. With increase in translucency there was noted a marked change in color from yellowish to bluish white, particularly in ware that was burned under reducing conditions, although this was also observed in the ware fired under oxidizing conditions.

The addition of small amounts of magnesite or dolomite is beneficial in many ways, particularly to those bodies which should mature at from cone 10 to 11.

Special Bodies.

In view of the fact that hard-fire porcelain bodies develop more or less well-defined crystalline sillimanite, it was decided to replace all of the quartz in some bodies by artificial sillimanite—a mineral having a low coefficient of expansion and not subject to crystalline transformations as is the quartz. The sillimanite calcine was prepared in several ways but the most satisfactory procedure was to calcine a thoroughly blended mixture of 258 parts of kaolin and 102 parts of anhydrous alumina. These constituents were ground dry in a ball mill with 2 per cent by weight of powdered boric acid, mixed with water, pugged into a stiff mass, and then molded into small lumps about an inch or two in diameter. These were calcined to cone 20. The boric acid accelerated the reaction and apparently did no harm—probably volatilizing at a fairly low temperature. The calcined material was ground dry to pass a 100 mesh sieve and was then introduced into the body in the same manner as the other materials.

A petrographic examination of the calcine showed the presence of about 10 per cent of large sillimanite crystals (0.01 to 0.03 mm. long), 40 to 50 per cent of the ground mass being weakly bi-refracting and probably composed of very minute sillimanite crystals too small for accurate measurement. There were also traces of what appeared to be a minute amount of uncombined Al_2O_3 .

A body having the following composition was prepared:

Body No. 50.

Sillimanite calcine.....	22.5 per cent
Kaolin.....	51.0 per cent
Feldspar.....	25.0 per cent
Whiting.....	1.5 per cent

100.0

The burning range is shown by the curve in Fig. 13 and requires no explanation. Its long temperature range should be noted. The sillimanite having been introduced in the place of flint, the body is free from the strains due to volume changes caused by the



FIG. 13.

transformation of quartz. Sillimanite has proven useful in the preparation of bodies of different compositions—particularly where a low coefficient of expansion is desired. It is to be hoped that natural deposits of this mineral will be found in quantity. It has also been found that the sillimanite calcine may be incorporated with the flux used in the body—which makes it possible to reduce the calcination temperature to as low as the softening temperature of cone 14. A natural deposit, however, would be ideal for use providing the content of iron oxide were sufficiently low.

Cone 11 Bodies.

A number of the bodies in the field covered are within the range of commercial bodies fired from cones 10 to 12, even though the clay content be as high as 60 per cent. All things considered, the range of body composition for ware fired to from cones 10 to 12 (such as hotel china) would lie between the following limits:

Flint.....	30	to 40	per cent
Feldspar.....	14	to 18	per cent
Alkaline earth fluxes.....	4.0	to 0.5	per cent
Ball clay.....	3	to 8	per cent
China clay.....	45	to 25	per cent
Florida clay.....	10	to 6	per cent

It is evident, of course, that it would not be permissible to use a high feldspar content together with a high alkaline earth content. Dolomite is found in nature sufficiently pure for use in pottery bodies and can be secured at a very low cost. The lime, magnesia, or dolomite fluxes are of considerable aid in securing a whiter color.

Florida kaolin may be used to a certain extent as a substitute for ball clay, but should not be depended upon entirely in the manufacture of thin or medium-weight ware.

The limits given for ball clay are lower than some potters are probably using but they are as high as is necessary under working conditions where reasonable care is used. This statement is made after careful consideration and actual knowledge of the working qualities of such bodies.

Color.

In many wares, and particularly in table wares, color is one of the most important factors connected with their sale and must receive serious consideration. Sometimes other qualities must be sacrificed in order that the color may be as nearly white as possible. This is to be regretted but must be contended with as long as the trade demands it. Some of the most beautiful ware made in America is cream colored and is finding a large market. There is nothing more pleasing than cream-colored ware and it is a mystery as to just why china should be white.

There are three ways of securing white porcelain: first, the use of very pure materials; second, burning under reducing conditions; and third, masking the yellow color with a blue stain. The first method is ideal but practically out of the question. However, the purity of all materials must be considered and the quality maintained at as high a standard as the grade of ware will warrant.

As previously stated, the addition of small amounts of alkaline earth fluxes, such as dolomite, magnesite or whiting, improves the color regardless of any other treatment the body may receive.

The second method is largely used in Europe and when properly carried out results in a purer white than is produced by a stain. The ferric oxide is reduced to the lower oxides which, owing to their dark color and fineness of grain, produce a whiter effect. Care must be taken to start the reduction at a sufficiently low temperature so that the reducing gases may penetrate the structure completely and thus bring about the desired effect. The bisque burn is carried to a low temperature and the glaze burn brought to maturity in the following way: The burn is divided into three parts, *viz.*, the heating-up period, the reducing period, and the finishing period. Oxidizing conditions are maintained during the heating-up period—which extends from the beginning of the burn to the softening point of cone 09.

The reducing period extends from cone 09 to cone 8—the latter point depending somewhat upon the constitution of the body and of the glaze. During the reducing period, carbon monoxide and hydrogen should be present in the kiln gases in quantities from 3 to 5 per cent. Too heavy reduction should be avoided. If

reduction is too strong when the glaze begins to soften and the body begins to tighten up, the ware may be spoiled by the deposition of carbon in the body or softened glaze.¹

The third procedure, the use of cobalt stain, represents the familiar effect of the bluing used in washing clothes. It is evident that the use of one color in order to mask another cannot be as satisfactory, as far as quality of shade is concerned, as the total elimination of the yellow color. However, for ordinary purposes, the difficulty of securing proper reduction warrants the use of a stain. The cobalt is preferably introduced as the precipitated basic carbonate (obtained by the addition of sodium carbonate to a solution of cobalt salt), followed by one or two washings by decantation. The precipitated carbonate must then be ground into the body in a ball mill. It may also be introduced into a body in a blunger but this practice is not as satisfactory.

In conclusion the writers wish to express their appreciation to Mr. A. V. Bleininger for advice in outlining the work and to the force of the Clay Products Division of the Bureau of Standards for a great deal of assistance in carrying on the experimental work.

¹ For complete description see G. H. Brown, "Burning of Porcelain," Proceedings New Jersey Clay Workers' Association, 1914.

THE USE OF CAR TUNNEL KILNS FOR BRICK AND OTHER PRODUCTS OF CRUDE CLAYS.

By ELLIS LOVEJOY, E.M., Columbus, O.

There are a number of problems in car tunnel kilns which must be solved in order to adapt the kiln to common clay products.

A major problem is to distribute the heat uniformly among the ware. The ware is in relatively small units but each unit comes in close contact with the furnace.

In large down-draft kilns the ware placed around the bags where the flame strikes it is largely rejected or at best it goes into second quality or culls. There would exist the car tunnel kiln problem in down-draft kilns if the kilns were built four to six feet wide with the bags removed and the ware set in small units in front of the furnaces. We would have then about one thousand bricks with a furnace on each side. How many of the bricks would be fire-flashed and overburned? Suppose we are burning face bricks, what percentage of product with uniform or satisfactory color would be obtained? Color is a very sensitive test of combustion conditions. Paving bricks are also very sensitive to heat conditions. Many factories cannot produce No. 1 quality bricks around the bags and over the top of the kiln, but in a down-draft kiln the percentage of these second quality bricks is relatively small. What would be the result if fifty or more per cent of the product is exposed to the flame?

Pottery, in the manufacture of which the car tunnel kiln is making rapid progress, is placed in saggars and the walls thereof interpose between the flame and the ware. Moreover, the size and shape of the saggars are such as to provide large spaces for the circulation of the air and gases. In some operations it is customary to set bisque on top and glost at the bottom, thus taking advantage of difference in temperature, and such difference in temperature is not serious.

Bricks, however, are set in close checker work and it is difficult to distribute the heat uniformly through the mass.

We cannot set bricks vertically around the tops of the bags in down-draft kilns because the greater shrinkage on the flame face will cause the face to draw over and fall into the bags, followed by a second and a third face as they become exposed to the flames. We must, therefore, rack back the bricks on cars as we do around kiln bags, and if we do this where are we to get any high-grade face bricks which must be perfectly faced in the setting? Some hollow tiles made from high shrinking and low burning range clays are badly warped and misshapen where the flame strikes them and the loss of ware would be serious if the flame struck the bulk of the mass.

Any cull brick pile will contain bricks much smaller on one end, due to the fact that the small end was exposed to flame, as in the arches of up-draft kilns. Under such conditions there is a marked difference in color, size, and hardness in eight inches in length. Would the conditions in a car tunnel kiln be equivalent to those in the arches of an up-draft kiln?

In three designs of car tunnel kilns the combustion takes place in a box or flue on each side of the kiln and the heat conducted through the walls of the flues is carried to the ware by circulation of air around the combustion flues thence over and down among the ware. In two kilns the operation is regenerative—the air after passing among the ware re-circulates around the combustion flues. In two other designs the operation is that of a down-draft kiln in which the combustion gases rise through a bag and descend among the ware and are drawn through a perforated floor into the next compartment and continuing until finally drawn from the kiln. In the other designs the cars of ware simply pass a flaming furnace sometimes with an intervening flash or perforated wall. There are then three types of car tunnel kilns—direct heating, indirect heating in the tunnel, and compartment operation.

One direct-heating type sets a combustion arch transversely of the car in the bottom of the ware comparable with the arch in an up-draft kiln and this arch, being built of fire bricks and retained as a permanent part of the car furniture, should give better results than those from the arch of an up-draft kiln. The indirect-heating types would seemingly better solve the flame

difficulty, although the compartment type appears advantageous and may prove very efficient when it is successfully developed and adapted. Unfortunately, one of the compartment type was not successful in an initial installation, but one must not conclude that the type is not promising because of this single failure.

There have been many failures of the direct-fire tunnel types in the past, yet new designs are constantly coming and proving successful in some lines of ware.

Manufacturers of common wares will have to be shown that simply pushing cars of ware through a fiery furnace will give satisfactory results:—namely, freedom from fire-flashing; uniformity in color, size, and hardness; no warping and no fire-cracking.

Assuming that the flame difficulty may be overcome in some types of kiln, there remain the racking back, complex bonding to insure the stability of the mass of ware and to provide circulating flues.

Such setting is serious in face brick manufacture and may be objectionable in other common wares. Drain tile, for instance, does not lend itself readily to complex setting, and it is not desirable to have transverse or longitudinal flues in the ware.

The manufacture of common wares is regarded by many ceramists as a job requiring little intelligence, but as a matter of fact the common ware manufacturer has to overcome the most difficult problems. He is dealing with a single raw clay with all its inherent difficulties which must be overcome in a large way in every step of the process of manufacture, while the manufacturer of other wares is dealing with a synthetic body and is incompetent if he cannot improve on natural clays.

One of the problems in a car tunnel kiln is to protect the cars from the heat. Sand seals on the sides and tongued and grooved end-locks in the car frame, or furniture, shut off the cars from the heat tunnels fairly well but not perfectly and they do not overcome conduction. Two designs do not even use sand seals and the car simply projects into a recess in the side wall, at best offering but slight resistance to the upward passage of air. In practically all designs there is some method of cooling the under tunnel and thus protecting the cars. One cools the cars by air pipes along the tunnel walls adjacent to the car structure. This

is an indirect way of cooling by means of which there is theoretically no air circulation in the tunnel under the car floor and the only air which could get into the upper tunnel from the car space would be that from leakage. Another design has a duct under the cars which may be closed and the only air admission is that from leakage. Dampers in the bottom of this duct may be opened and any amount of air allowed to enter. The amount of air which is allowed to enter is that required to keep the cars cool, and this air circulates around the car structure and rises into the heat tunnel, there being no sand seal. A third design introduces the air under pressure through pipes and jets the air against the car structure at intervals in the hot zones. Again we have direct provision to draw the air through the car duct and deliver it under the furnace grates or to the gas burners, usually a free circulation under the cars but in one instance through a sheet metal casing, thus cooling the cars indirectly.

It matters not how it is accomplished, the cars must be cooled and there is more or less air finding its way up around the cars and enveloping the ware.

Let us consider a down-draft kiln in this light. Suppose we circulate cold air under the kiln floor and allow it to seep, or freely flow, into the kiln on the inside of the wall at the floor level. Every down-draft kiln burner knows, or should know, that chilling the kiln bottom results in serious loss in the bottom ware. A prominent company several years ago put flues under the kiln floor through which air was to be taken from the outside, under the kiln floor, heated by conduction from the waste combustion gases, then back to the furnace for primary combustion. The purpose was to heat the air for combustion which it accomplished, but at the same time cooled the kiln bottom to the extent of serious effect on the ware and the scheme had to be abandoned, as have several other similar schemes.

Dampness under the kiln has the same cooling effect on the kiln bottom in consequence of evaporation and many manufacturers have experienced trouble and losses on this account. Common wares cannot be burnt satisfactorily in either down-draft or continuous kilns if the kiln floor is chilled and, particularly with some short-burning range clays, the effect would be to quickly

put a profitable business into the hands of a receiver with an ultimate sale of the plant for junk.

The car tops are cooled and the best of insulation is not the equal of a blanket of high temperature combustion gases under the kiln floor. In the combustion zone we have in the direct-fire kilns combustion gases rising in the space between the ware and the flash wall of the furnace. We also have a current of cold air from under the cars creeping up the face of the ware, taking heat from the bottom ware and carrying it to the top and finally commingling and combining with the furnace gases in secondary combustion, thus still further increasing the temperature on top.

There are many clays, particularly limey clays, and some vitrified products, which cannot be profitably burned if the variation in kiln temperature exceeds 60°C . —three cones. This can be done commercially in down-draft kilns. We say "commercially" with a purpose. There can be obtained the same cone temperature in top and bottom of a down-draft kiln but at such fuel expense as to rule it out as a commercial operation. What can be done commercially in a car tunnel kiln? Certain reports indicate the same temperature throughout the mass of ware. This sounds encouraging indeed, but is it true? The manufacturers of crude clay wares wish to know and are greatly interested. There are also reports that common ware on the face of the cars is vitrified, or at least extremely hard, while that in the bottom center is barely within the limit of salable building bricks. This does not check with reports previously mentioned. Some kilns are burning all biscuit and others all glost, but what variations in temperatures will these wares stand? One kiln, at least, burns bisque on top and glost in the bottom to take advantage of the difference in temperature.

L. E. Barringer¹ states that, "the kiln at Schenectady is used in firing porcelain insulators to a temperature of 1300 to 1400° C." A variation of 100 degrees in a four-foot column of common ware in many instances is prohibitive.

It is frequently necessary to get within 60 degrees in a ten-foot column of ware, and it is desirable to do better. Even this variation, in a four-foot column, would give too much difference in

¹ *Trans. Am. Ceram. Soc.*, 18, 118 (1916).

color, size, and degree of vitrification to be satisfactory. In effect, the product would be practically all "bag" bricks, since we cannot encase our common wares in saggars.

Common wares are often quite wet when set in the kilns. They should not be, of course, but they are, and in consequence require careful water-smoking, which is particularly true of dry-pressed bricks requiring from three to eight days of slow water-smoking. Will the car tunnel kiln be adapted to this product?

Many common clays are high in carbon and iron sulphide, as for example the black lignitic clays in New Jersey and the black Ohio shale. The oxidation of these is a serious problem. How will it be worked out in the car tunnel kiln?

One might assume that we are opposed to the car tunnel kiln, but, quite the contrary, we are very much interested in its success and when we are shown that it will advance the manufacture of common clay wares, we will boost it to the limit.

The car tunnel kiln is a century old and more, and there are many wrecks strewn along the wayside. In the present revival, the kiln has come to stay, but there are a number of problems which must be solved to adapt it to the successful production of common clay wares.

We have not a complete list of the car tunnel kilns in this country, but there are over forty under construction, in operation, or abandoned.

So far as indicated by available records there are fifteen under construction and in operation on white-ware, porcelain, etc.; there are five burning refractories; two on building bricks; seven abandoned as failures. There are also several in other industries, —burning carbons, annealing, etc., about which we have no information.

There are more than a dozen kilns in this country devised by different inventors, from which the clay workers may choose. Of these, at least ten have been tried out, or are under construction. Two types have the credit of twelve or more kilns each in this country. This shows the marked interest in the car tunnel kiln.

The kiln is rapidly being given the opportunity to prove its merits, but much remains to be done to adapt it to the several

distinct lines of ware before it can take its place alongside of, or displace, the other types of continuous kilns.

COMMUNICATED DISCUSSION.

L. E. BARRINGER: The author has clearly pointed out some of the difficulties which might be anticipated in attempting the use of continuous tunnel kilns in the burning of products made from crude clays, as structural and paving brick, drain tile, etc.

The first criticism which is made is that of possible lack of a sufficiently uniform temperature in the continuous kiln and the difficulties of properly distributing the heat through the ware as the latter passes through the combustion zone. It is pointed out that the nearness of crude clay wares to the throats of the fire boxes in all types of kilns leads to fire-flashing, overburning and shrinkage differentials, and it is the author's opinion that a very much larger percentage of the product would be subjected to overfiring, through nearness to the fire boxes, than in the large periodic (and principally down-draft) kilns commonly employed for the firing of the crude clay wares.

Exposure to the direct flame of the furnace is of course productive of high losses and the author's question as to what would be the result if 50 per cent or more of the product should be exposed to the flame, might be answered by saying that the result would probably be a loss of high-grade ware to the extent of 50 per cent or more. But there should not be such a high percentage of ware exposed to excessive temperature and I believe that the distribution of temperature can be controlled within closer limits in a properly designed tunnel kiln than in a large periodic down-draft kiln.

Unfortunately, my statements¹ of temperature distribution in connection with the tunnel kiln in use in the Porcelain Department of the General Electric Company were perhaps not made sufficiently clear. In the paper in question it was stated that "the kiln at Schenectady is used in firing porcelain insulators to a temperature of 1300 to 1400° C" which was intended to mean that the maturing temperature of porcelain was always between these limits, that is, some porcelains were fired at a little higher

¹ *Trans. Am. Ceram. Soc.*, 18, 118 (1916).

temperature than others. A little later in the same paragraph, however, the statement is made "a uniformity of distribution of temperature is secured of well within one cone." This means that whether the porcelain is fired at 1340°C or 1380°C , the actual differential at the proper maturing temperature can be reduced to within 20°C . For instance, if the maturing temperature is 1340°C , the temperature in all parts of the firing zone of the continuous kiln can be maintained within the limits 1330 to 1350°C .

In the same paper the writer made the statement that for brick and crude clay wares, the necessity of uniform temperature is not as great as in the higher-grade clay wares, since matters of porosity, exact size and uniform color are not as important. I think the author of the paper under discussion confirms this in stating that there are many common clay products which cannot be profitably burned "if the variation in kiln temperature exceeds 60°C (3 cones)." This is decidedly more than the one cone or 20°C which is required in the firing of such ware as electrical porcelain and which is maintained in the tunnel kiln being operated at Schenectady.

There would seem to be no fundamental reason why the crude clay wares cannot properly be protected from fire-flashing and over-burning in a continuous tunnel kiln if the fire boxes and fire zone are properly constructed. Inasmuch as the temperatures required in firing brick and similar products are not as high as those necessary for the firing of porcelain, the fire boxes can be placed at a greater distance from the tunnel of the continuous kiln at the firing zone without excessive loss of heat.

A second point that the author brings out is the uncertainty of being able to regulate the condition of the fire gases and to bring about oxidizing or reducing conditions as required. This, however, can be done, although it must be admitted that a continuous kiln from its very nature cannot be as quickly manipulated in this respect as a periodic kiln and the changes from a reducing fire to an oxidizing fire or *vice versa* require longer periods. Such control can be obtained, however, either in the open tunnel kiln, as the Didier-March, or in the muffle kiln, as the Dressler.

In discussing the matter of protecting the cars by sand seals

and otherwise, and in considering the possibility of air leakage which should tend to cool the floor or bottom of the kiln, the author fears that such cold air leakage will materially affect the temperature of the ware at the bottom of the kiln. In this connection, however, it is to be pointed out that the very point where such air leakage might take place is at the point of maximum temperature, that is, between the face of the ware and the ports from the fire boxes, so that slight air leakage might possibly do more good than harm. Of course, if such leakage is excessive, it may be injurious, both to the under-structure of the car and to the ware upon the car. If the writer understands the paper correctly, however, the direction of cold air leakage is considered as upward, whereas designers of kilns with sand seals undoubtedly assume that the leakage will be downward into the subway beneath the cars and the sand seal is particularly necessary to prevent the under parts of the car becoming so overheated that they are not as readily operated, to say nothing of the rapid deterioration of the iron and steel under such conditions.

It seems to the writer that of the difficulties which have been pointed out by Mr. Lovejoy, the most troublesome to meet successfully would be (a) the proper "water-smoking" of crude clay wares, (b) the handling of highly carbonaceous, calcareous and pyritic clays, and (c) the control of kiln gases, within sufficiently short time periods.

The designers and builders of continuous car tunnel kilns will probably desire to discuss the proper construction and method of handling such kilns when the burning of crude clay ware is involved and to answer some of the pertinent inquiries which Mr. Lovejoy has made.

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THE PRESENCE OF IRON IN THE FURNACE ATMOSPHERE AS A SOURCE OF COLOR IN THE MANUFACTURE OF OPTICAL GLASS.

By EDWARD W. WASHBURN, Urbana, Ill.

It is well known that the presence of very small quantities of iron in glass imparts to it a greenish color. In the common varieties of glass, this color is usually eliminated by employing a "decolorizer" which produces the complimentary color. However, this procedure is not possible in the case of optical glass owing to the decreased transmission of light which accompanies it. For this reason each material employed in making up the batch for producing optical glasses must have an extremely high degree of purity as regards its content of iron.

The coloring effect of iron seems to be especially pronounced in the case of the flint glasses, and the glasses of this type hitherto manufactured in this country for optical purposes all have a very evident greenish tinge and this in spite of every precaution to employ only the purest materials. The writer's attention was first directed to this situation by the results obtained with some experimental melts of a heavy flint glass ($n_D = 1.64$) obtained in an electric furnace. These melts were entirely free from any trace of color, although the same batch when melted in the same type of pot in a gas-fired furnace invariably gave a product having a decided greenish color.

The pots in both cases were kept carefully covered during the melting and the other conditions in the two experiments were such that the only possible source for the color obtained with the gas-fired furnace seemed to be the presence of iron in some form in the atmosphere of the furnace. An opportunity to further test this hypothesis was afforded the writer by Mr. A. V. Bleining, of the Bureau of Standards. The tests were made on one of the large pot furnaces of the Bureau's optical glass factory at Pittsburgh and were conducted in the following manner:

A five-foot fused silica tube, open at both ends, was inserted

through the wall of the furnace so that the end of the tube was immediately above the pot of melted glass. The temperature of the furnace was approximately at the maximum point attained during the manufacturing operation, and was just immediately preceding the period at which stirring was begun. The outer end of the tube was connected to a glass tube ending below the surface of a dilute solution of sulphuric acid contained in a wash-bottle. Suction was applied to the wash-bottle so as to draw a stream of the furnace gas through the sulphuric acid. The experiment was continued for two hours, at the end of which time the silica tube was removed and washed thoroughly on the inside with some of the sulphuric acid from the wash-bottle. The acid was then tested for iron in the usual way with a solution of ammonium sulphocyanate, and a distinct positive test was obtained.

This experiment clearly demonstrated the presence of iron in the furnace atmosphere and rendered it extremely probable that this constituted a significant source of the color in the glass. This was further confirmed by the fact that, previous to stirring, a sample of the glass removed from the pot had a much better color than was the case after the pot had been stirred for a number of hours. Evidently, the iron taken up from the furnace atmosphere was mixed throughout the glass by the process of stirring.

The iron in the atmosphere was doubtless present in the form of ferric oxide, but whether the oxide was present in the form of a fine dust or in the form of vapor was not definitely determined, although it seems reasonable to believe that at the temperatures attained in the furnace, ferric oxide might have a sufficiently high vapor pressure to produce the observed results. However, it is hoped to settle this question definitely by attempting to directly measure the vapor pressure of ferric oxide at high temperatures.

Two obvious sources for the iron in the furnace atmosphere were: (1) The iron burners which extended far enough into the furnaces so that the ends were covered with a coating of the oxide; and (2) the iron content of the fire-brick lining of the furnace. In order to remove these two sources of contamination,

the iron burners were replaced by burners made of clay and the interior walls of the furnace were covered with a coating of kaolin. As a result of these changes in the furnace, Mr. A. E. Williams, Superintendent of the Pittsburgh Optical Glass Plant, reports that a distinct improvement in the color of the heavy flint glasses has resulted.

It was noted that the layer of white kaolin which was placed on the interior walls of the furnace gradually acquired a red color, either by the absorption of iron from the brick behind it or by the taking up of iron from the furnace atmosphere.

The results of the above experiments demonstrate very clearly that in the construction of furnaces for the manufacture of optical glass it is highly desirable to exclude all materials which will give up iron to the atmosphere of the furnace. The interior of the furnace should, if possible, be lined with a course of kaolin bricks, and if it is necessary to employ any object constructed of metallic iron for any purpose *in the interior* of the furnace, water cooling should be employed to prevent volatilization of the iron.

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THE CONTROL OF THE LUSTER OF ENAMELS.¹

By HOMER F. STALEY, Washington, D. C.

Crystallization.

When melted, glasses are true solutions, corresponding in all respects to solutions of salts and water at ordinary temperatures. When these molten solutions are cooled, we would expect them to turn gradually to a mass of crystals, just as an aqueous solution of salt does if the temperature to which it is cooled is sufficiently low. The only difference is that the glassy solutions should crystallize at higher temperatures. The temperatures at which glasses would become completely crystallized, if sufficient time were allowed, vary from 550 to 1100° C, yet in practice they are cooled and exist permanently at atmospheric temperatures without any crystallization taking place. In this condition they are still true solutions—differing from aqueous solutions only in being so viscous that they are rigid. All bright finish enamels, glasses and glazes may be regarded then as undercooled liquids. The tumblers from which we drink are in a sense just as truly liquids as the water they contain.

Of course, if the constituents of a glass crystallize, the surface becomes mat instead of bright. Since bright finish enamels are the type desired for enameling metals, the enamel maker must so compound his enamels that they will not crystallize when subjected to the normal working and cooling conditions of enameling shops. Fortunately, the sudden cooling to which enameled ware is subjected is not favorable to crystallization. On the other hand, the working temperature is so low that the glass is easily saturated by the compounds formed in the molten magma by some of the oxides used. Just as a hot, saturated, aqueous salt solution tends to become supersaturated and to deposit crystals of the salt on cooling, just so does a hot, saturated glass or enamel solution tend to deposit crystals when it is cooled.

Effect of Viscosity.

The most simple method of overcoming the tendency to crystal-

¹ By permission of the Director, Bureau of Standards.

lize is to make the enamel viscous at the temperatures at which crystallization takes place. In even a moderately viscous liquid, it takes considerable time for crystallization to start and the rate of growth is slow. Since enameled iron ware is cooled so rapidly, sufficient time is not given in the cooling process for an appreciable formation of crystals in a viscous enamel, unless the tendency for deposition of crystals is very great.

Silica alone melts to a very viscous glass, and, in general, the addition of silica to any melt increases the viscosity. Silicates high in silica also melt to viscous glasses. If silica (flint), sand or feldspar (a high-silica compound) is added to an enamel, the glass is rendered more viscous at all temperatures, and the tendency to become dull from crystallization is lessened. Since the working temperature of the enamel is raised by this procedure, this method has but slight application in controlling the viscosity of enamels that must mature at temperatures rather rigidly fixed by shop practice and working conditions.

Boric oxide alone forms a very viscous glass at low temperatures; but, as shown by the writer,¹ the viscosity decreases rapidly as the temperature rises. The glass was found to be three times as viscous at 750° C as it was at 1000° C. The first temperature approximates that at which crystallization takes place in enamels, and the second is near the maturing temperature of most enamels for cast iron. The borate glasses of any given base resemble silicate glasses in behavior and become more viscous as the percentage of boric oxide increases. The following results were obtained for barium oxide—boric oxide glasses:

Per cent B ₂ O ₃ .	Per cent BaO.	Relative viscosity at the same temperature.
20	80	3.05
25	75	3.18
30	70	3.35
35	65	3.52
40	60	3.70
45	55	4.02

It is noteworthy that the presence of compounds and eutectic compositions produced no noticeable effect on the viscosity curves.²

¹ "The Viscosity of Molten Glasses," Original Communications, *Eighth International Congress of Applied Chemistry*, 5, p. 127.

² Cf. *Trans. Am. Ceram. Soc.*, 13, 675 (1911).

The viscosity of borate glasses decreases with rise of temperature in the same general way as that of fused boric oxide, but not as rapidly. The effect of increasing the boric oxide in cast iron enamels is to increase the viscosity at the temperatures at which crystallization is liable to take place, and thus to decrease the tendency to mattness. Its effect differs from that of silica in that the maturing temperature is not raised but, in the case of many enamels, is actually lowered.

Kaolin (china clay) has a very decided tendency to raise the viscosity of enamels but is not much used in American although found in some German formulas. Any material which does not fuse or go into solution in the enamel, such as most metallic oxides added as opacifiers, makes the enamel more viscous. Decrease of any of the fluxing oxides, except boric oxide, makes the enamel more viscous. Therefore, viscosity may be increased by decreasing any of these. Decrease of fluorides has the same effect.

Effect of Concentrations.

With the exception of boric oxide, all of the materials in enamel compositions known as fluxes, *i. e.*, the oxides of lead, zinc, sodium, potassium, calcium, barium, magnesium, and the various fluorides, tend to form compounds which are easily crystallizable. Lead oxide differs from the others in that its compounds when melted alone do not crystallize until very low temperatures are reached. Lead silicates do not crystallize until temperatures of 750°C or lower are reached,¹ and lead borates have even lower crystallization temperatures. Since normal enamel compositions are too viscous at low temperatures to allow crystallization to take place, lead compounds do not crystallize from enamel glasses. Therefore, lead oxide shares with boric oxide the distinction of being a flux and yet not producing a mat finish when present in the enamel composition in large amounts.

Of course, the tendency for any compound to separate in the crystalline form from a cooling glass is decreased by decreasing the amount of the compound in the glass. Therefore, the amount of each of the fluxes, except boric oxide and lead oxide, should be kept low. This means that as the total amount of these crystall-forming fluxes increases a greater variety must be used.

¹ Cooper, Shaw and Loomis, *Am. Chem. Jour.*, 1909, p. 461.

The effect of concentration of various fluxing oxides is shown by the series of enamels described below. As the basis of the series, the following batch was taken:

Raw.	Melted Percentages.
Potash feldspar.....41.0	26.5 silica
	7.5 alumina
	7.0 potassium oxide
Borax.....24.6	9.0 boric oxide
Sodium nitrate.....2.7	5.0 sodium oxide
	4.8 aluminium fluoride
Cryolite.....12.0	7.2 sodium fluoride
Tin oxide.....8.0	8.0 tin oxide
	75.0 constant
	25.0 variable
	100.0

The composition of the 25 per cent variable part and the luster of the resultant enamels is indicated in the accompanying table:

TABLE SHOWING EFFECT OF COMPOSITION ON LUSTER.

Num- ber.	Na ₂ O from soda ash.	BaO from barium carbon- ate.	CaO from calcium carbon- ate.	ZnO from zinc oxide.	PbO from red lead.	B ₂ O ₃ from boric acid.	Luster.
1	25						mat
2		25					semi-mat
3			25				not melted
4				25			mat
5					25		bright
6						25	bright
7	12.5	12.5					semi-mat
8	12.5			12.5			mat
9	12.5					12.5	semi-mat
10		12.5		12.5			semi-mat
11		12.5				12.5	bright
12				12.5		12.5	bright
13	8.33	8.33		8.33			oily
14		8.33		8.33		8.33	bright
15	5.00	8.33		8.33	3.33		bright
16	5.00	8.33		8.33		3.33	bright

Enameling Technique.

Any necessity for prolonging the enameling operation that involves partial cooling and reheating of the enamel after the coat is matured furnishes favorable opportunity for the development of crystallization and dull finish. Therefore, considerable care must be taken to avoid all necessity for patching by having the metal in the best possible shape for enameling before the operation commences, and by employing the most skilful workmen to apply the enamel.

Sulphur Compounds.

It is well known that sulphur compounds in an enamel tend to separate on the surface in feather-like crystals, causing a diminution of luster. While this may be due to sulphur in the enamel materials, and the presence of sulphur in these should be avoided, it is not probable that enamel compositions made from the grade of chemicals commonly employed contain enough sulphur to cause the trouble. Seger has shown that a glass can contain 2 to 4 per cent of sulphur trioxide and still be perfectly clear.¹ It is interesting to note that when Seger made a melt from sodium carbonate, barium sulphate and silica, the glass gall, which separated when an excess of sulphur was present, consisted of sodium sulphate, not barium sulphate as might be expected from the strong affinity of barium for sulphur at low temperatures. In fact, glass gall from common glasses ordinarily consists largely of sodium sulphate. Mellor² records experiments in which ordinary pottery glazes were found to dissolve comparatively large amounts of various sulphates, such as those of barium, calcium, lead, sodium, and potassium, without showing any ill effects. An experienced enamel mixer informs me that he once had a separation of sodium sulphate in the form of glass gall in considerable amount from an enamel batch in the melting tank. In grinding this batch he mixed the glass gall with the good glass and got satisfactory ware from the mixture. Mellor believes that the feathering of pottery glazes by sulphur is due to the satura-

¹ "Collected Writings of Herman A. Seger," p. 646. Published by Am. Ceram. Soc.

² J. W. Mellor, "Clay and Pottery Industries," Vol. I, p. 63, published by Chas. Griffith and Co., London.

tion of a surface film of the glaze by sulphur in the kiln atmosphere. This is probably the case in enamels also, for it occurs most frequently when a sulphur-bearing fuel is used for heating the enameling furnaces. A number of enameling plants experienced difficulty from sulphur feathering when they changed from the use of natural gas to bituminous coal. The trouble is much less common when well-ventilated muffles are used than when the air currents in these are sluggish. Cracks in the floor of the muffle which allow the products of combustion to leak in are a common cause of sulphured ware. Open-arch or semi-muffle kilns are prone to produce ware of poor gloss unless a strong draft is used so as to keep the flame hugging the roof of the furnace.

Sometimes quicklime is placed around the inside of the muffle against the walls, in the hope that the quicklime will absorb the sulphur. This is generally not very effective. In the first place, it is only rarely that the sulphur-bearing fumes pass through or over the quicklime unless it is placed directly over a crack or hole. The lime does not attract the sulphur from the kiln atmosphere as a whole. In the second place, if sulphur-bearing fumes do come in contact with the lime, it soon becomes saturated and should be replaced much more often than is the common practice. One per cent of volatile sulphur in a ton of coal will give 40 pounds of sulphur dioxide or 50 pounds of sulphur trioxide, either of which will neutralize 35 pounds of quicklime if brought into intimate contact with it. It sometimes pays to pile quicklime over a temporary patch in the floor of a muffle, but even then the lime should be changed daily.

Index of Refraction.

Aside from the question of glasses being dulled by the presence of crystals or sulphur compounds on their surfaces, the brilliance of the glasses themselves will vary. The brilliance of a glass is measured by its refraction for light, the higher the index of refraction, the more brilliant the glass. In any one class of glasses, the index of refraction is higher the greater the density of the glass.¹ Since lead oxide, barium oxide and zinc oxide tend to

¹ H. Hovestadt, "Jena Glass," pp. 388-393, published by The Macmillan Co., New York.

produce very heavy glasses, they also produce glasses of great brilliance. Potassium oxide makes more brilliant glasses than sodium oxide, and the substitution of boric oxide for silica makes more brilliant glasses, although the density of the glass is lowered slightly. High-flint enamels are generally more brilliant than those in which feldspar is the only refractory.

COMMUNICATED DISCUSSION.

E. P. POSTE: We were very much interested in the remarks under the heading "Sulphur Compounds," in which Mr. Staley has referred to the presence of sodium sulphate on the surface of enamels, introduced by sulphur in the raw materials entering into the enamel mixture or by sulphur gases in contact with the enamel during burning.

We have carefully studied this particular type of trouble under two different sets of circumstances in connection with steel enamels applied by the wet process.

The first instance came to our attention while endeavoring to work, on a semi-commercial scale, an enamel which, through the experimental stages, had been very difficult to bring to a proper condition for spraying. The clays which were in use in "setting up" commercial formulas at that time did not properly suspend the enamel in question—without the addition of an amount which caused a definite dullness of the surface. Using less clay, it was necessary to add such an excessive amount of magnesium sulphate solution as a vehicle that a very definite sulphur scum was produced.

The other instance in mind came to our notice while we were endeavoring to burn commercial formulas on an experimental scale in a small furnace which was being fired by producer gas under conditions such that the products of combustion came in contact with the enamel. This took place at a time when it became necessary to find a substitute for natural gas in firing a direct-fired enamel furnace. The natural gas had never given trouble from sulphur scum. The first producer gas used was made from a coal which contained 2.79 per cent sulphur and the second test was made with a gas made from a coal containing 0.77 per cent sulphur. In both cases there was a very definite sulphur

scum which did not appear immediately on cooling but which was very evident after 24 hours.

It is particularly interesting to note that in the several cases of scumming—due to magnesium sulphate and the producer-gas fuel—the sulphur scum was carefully tested and identified as sodium sulphate, a fact which confirms very definitely the statements of Mr. Staley and of the other authors to whom he refers.

THE ELYRIA ENAMELED PRODUCTS CO.
ELYRIA, OHIO.

OBSERVATIONS ON APPARENT CAUSES OF FAILURE OF LEAD GLASS POTS.¹

BY A. F. GORTON.

Introduction.

In order to appreciate the difficulty of building a satisfactory pot for melting lead glass, it is necessary for one to examine a number of pots after removal from the furnace, and to see for himself the many ways in which failure is possible. When one considers the unusual physical and chemical strains that a pot must withstand, it seems remarkable that more than a single melt is obtainable, yet 15 to 20 melts is only an average life, and even now, three years after the disappearance of the lamented German clay, records of 40 to 60 melts are occasionally encountered. A pot must be heated with intelligent care in the arch, or preheating furnace, and this by the way is no mean task when one considers the rather crude design of the arch, the inability to distribute the heat properly, and the constant temptation to hurry the pot into the furnace for the sake of maintaining production(!); secondly, the pot must be transferred to the furnace, and this cannot be accomplished under present-day methods without subjecting it to a certain amount of strain, partly mechanical and in part thermal. Once in the furnace, the pot is subjected to both physical and chemical strains: (1) the throwing in of the relatively cold (and sometimes damp) batch is a distinct shock, and must result in the formation of tiny surface cracks in the bottom, which widen as the glass works into them; (2) there is an erosion of the clay due to the boiling action and wash of the molten glass; (3) the hydrostatic pressure of the glass charge is sometimes sufficient, during the melting period, to cause the side walls to bulge outward or "belly." These are physical actions. The actual corrosion of the clay by the glass and especially the slagging action of iron may be cited as chemical causes of leaks in pots.

¹ Read at the meeting of the Northern Ohio Section of the American Ceramic Society, Cleveland, O., December 9, 1918.

While inspection of pots after they are hauled out of the furnace usually affords some ground on which to base an inference as to the probable cause or causes of failure, there are many phenomena noticed, at times in only one pot out of 20, at other times in a succession of pots, which baffle the combined efforts of glass-house manager and potmaker to clear up, and remain a puzzle. The discussion that follows is based upon the writer's observations and impressions gained in the examination of the remains of some used pots which were broken up under his personal direction at the Toledo plant of the Libbey Glass Co., and though the limited number of pots precludes any numerical generalizations as to the causes of failure, still it will serve as a satisfactory illustration of the types of failure commonly observed. Twenty-two pots in all were inspected, and it was found that the general defects could be listed as follows:

1. Pitting and corrosion of the bottom, resulting, in a majority of cases, in a leak at one point or another—particularly marked at the knuckle (or intersection of the walls with the bottom).
2. Cracking of the bottom, with no sign of corrosion save in the jaws of the crack. (It seems that the glass does not attack the bottom unless the smooth surface is broken through and the porous clay of the interior exposed.)
3. Crack in the side, extending clear through, causing escape of the glass.
4. Side walls scored or furrowed from metal-line down. This action probably starts from a rather deep crack.
5. Hole through the side. It may be found on either side, about twelve inches or more above the bottom. Horizontal openings, especially near the bottom, are not herein included.
6. Sides bulged. In some instances the pot is strained at the bulge to such an extent that a crack develops, letting the glass escape; at times a rip in the back accompanies the bulging. If the clay is not sufficiently refractory, the pot will squat or collapse, and this condition was not uncommon some years ago, when the necessity of seeking new mixtures of raw clays and new proportions of clay to grog was forced upon the potmaker.
7. Hole through the back. This occurs sometimes at a height of 12 to 15 inches, at times much lower.

8. Crack through the back. These cracks, like those in the side, are always vertical.

9. Cracking under the hood, resulting in a leak. This fault was noticed in 4 of the 22 pots, and is not altogether to be laid to carelessness on the part of the potmaker, as a mechanical strain is unavoidable at this point, due to the construction of the pot, which is not lessened by the fact that the hood is the coolest part of the pot in the furnace.

10. Cracking and caving in of the crown. The construction of the pot-furnace is such that the heat strikes against the crown and back of the pot. The temperatures reached at these points are undoubtedly as high as 2700°F. , as the clay is often blistered (overfired) on the surface, and beneath the surface has reached a glassy or "vitrified" stage. There is a gradual change in color from the back wall to the bottom, the black shading off into a reddish buff, and this into a very pale buff or cream color in the middle of the bottom. Corresponding to this change in hue there is a change in porosity, for the parts described, from 5 per cent to 25 or 28 per cent. From the value of the porosity, it is quite easy to calculate the maximum temperature attained at the point in question, after the temperature-porosity curve has been determined experimentally for the pot-clay. The effect of this severe heat is to flatten the crown, but it rarely causes a collapse. Cracks in the crown result probably from strains set up in drying the pot. The crown, being the thinnest portion of the pot (2 to 3 inches as compared with $4\frac{1}{2}$ inches in the bottom and walls), dries most rapidly, and, it seems, also cracks most readily. Then, too, it is hard for the potmaker, in shaping the crown, to pack the clay as firmly as in the case of the walls, upon which he can exert the unimpeded strength of both hands.

From glass-house reports covering a period of several months or a year, it is possible to gain an idea as to which types of failure are most frequent. The writer has gone over reports from the Libbey Glass Co. for the four months June–September of this year, in which a total of 379 pots are listed, and finds that 81 per cent broke in the bottom, 11 per cent in the side, and 6 per cent in the back. Of the 22 pots above referred to, 18 broke in the bottom,—or a percentage of 81—two in the back, and two in

the side. The agreement of the percentage of bottom breaks is a coincidence, but it shows clearly how the vast majority of pots fail. In the following discussion an attempt will be made to give the various possible causes of such leaks, with a view to explaining the difficulty, under present-day glass-house procedure, of remedying these defects through alteration of the ingredients or the proportions of the pot batch.

Bottom Leaks.—Taking up first the case of bottom leaks, it was noticed that 8 pots failed through cracking, and 10 through corrosion. Of the former, two gave one melt each and one gave no melts. In the last case there were two cracks running from front to back, exactly over the points where the pot is supported by the fork, when it is brought from the arch to the furnace, hence the explanation is evident. Since only one of the 8 pots was of long life (28 melts), it seems likely that cracking in such cases is due to strains set up (1) in drying the pot, (2) in the pre-heating period, (3) in transferring it to the furnace. As to the first cause, it may be stated that when the bottom cracks open in drying, the direction of the crack is always from side to side, *i. e.*, at right angles to the length. The writer, where possible, noted the direction of the cracks in the broken pots, and in the majority of cases they ran from front to back. This applies only to long cracks. Jenkinson and Marson,¹ from observations made at the works of the Edinburgh and Leith Flint Glass Co., Edinburgh, state that insufficient preliminary burning in the arch may result in a sudden shrinkage after setting in the furnace, and as the bottom is much cooler than the sides, owing to the conductivity of the bench supporting the pot, the excessive shrinkage of the walls may force the bottom upward into a concave shape, and thus crack it. While the writer has seen no trace of this trouble, it may be well to point out the possibility of a different source of trouble: distortion of the bottom by an uneven bed. This also was not noticed in the present work, as the bottoms of all of the pots were plane.

Corrosion.—Turning to the next point under discussion—failure of pots due to corrosion—mention was made of the fact that 10 pots of the 18 showed corrosion distinct from that which

¹ *J. Soc. Glass Tech.*, Sept., 1918, p. 175.

accompanies a mere crack. That is, an appreciable volume of clay had disappeared, mostly from the bottom. These pots had given from 2 to 67 melts, which is surely the extreme range of life. In 8 pots of the 10, close scrutiny revealed the presence of iron, which had worked into the crevices, slagging the clay and opening the way for the leak. It was also noticeable in the form of very dark green or black glass lining the sides of the hollow or crack. Invariably the iron found the lowest point in the bottom. This was true also of metallic lead, which occurred in only 4 pots. In all four pots black glass was present, and the drops of lead were always imbedded in a dark mass of slagged clay. This seems to show that there is a sort of reduction of lead silicate by the iron, forming ferrous silicate and metallic lead. Evidence of corrosion by the lead itself was lacking, since what was observed could be due to the action of iron. Greaves-Walker¹ states that in the reduction of ores in the assay crucible, lead-bearing ores are very corrosive on crucibles high in silica. As the Gross Almerode clay is very silicious, this may account for the opinion commonly expressed by glassmakers that the German clay dissolved rapidly and evenly in the glass (though without throwing stones).

Effect of Iron.—There are two ways in which iron may enter the glass: from the glass batch, and from the pot itself. As to the former, it should be pointed out that iron may enter as the metal itself, introduced purely by accident, it is to be hoped, or as a legitimate mineral constituent of the batch. (This statement applies with equal force to the clay.) As to the former, it may frankly be admitted that under present conditions iron may occasionally be introduced, whether as scale or broken parts from grinding and mixing machinery, carelessness on the part of workmen in leaving nails, knives, bolts, etc., around where they can be swept among the raw materials, or in other ways; and, once in the raw materials, it escapes detection until the pot is broken up. It has been the writer's experience that iron from such sources is far more likely to occur in the glass mix than in the pot clay. In the shaping of the pot, the clay is applied in such thin layers that detection of foreign matter is easy. *The prevention of iron in the glass mix can be accomplished only by screening and magnetic separation at the last possible moment before*

¹ *Trans. Am. Ceram. Soc.*, 12, 54 (1910).

introduction into the pot. That such precautions are ignored by the majority of glass-houses is an established and deplorable fact.

The percentage of iron as a constituent of the raw materials is of course very low in the case of the soda-ash, niter, sand, red lead and other substances entering into the glass, as compared with the pot clay, which may have an iron content as high as 2 per cent. From a study of the burned clay it is clear that only a small fraction of the iron occurs as a more soluble form (sulphide and oxide), the greater part being combined with the clay, presumably as a complex silicate, and evenly distributed throughout the mass; for the "iron spots" are widely scattered whereas the clay body is evenly tinged with a buff color. Analyses of the raw clay rarely show traces of sulphur. Now, if a considerable portion of the iron occurred as sulphide or oxide, the inner surface of the walls of the pot would corrode evenly and to a marked degree, and naturally the glass would always show a green color. It is a fact, however, that few spots dissolve markedly in the walls, and, on the other hand, in a number of cases where a considerable volume of clay had been removed from the bottom, there was no trace of anything but clear glass. When masses of clay are torn bodily from the surface and float in the glass as "stones," it always happens that the clay is imbedded in white glass. If iron were to pass into the glass as the clay dissolves, it becomes difficult to explain those cases of marked corrosion where iron is not observed. As the dark glass is always observed at the lowest points of the bottom, it is evidently dense enough to resist being swept upward by the boiling of successive melts. The hypothesis that iron is dissolved out of the clay is not supported by the evidence at hand. The extremely black color of the glass in the fissures, the slagging of the clay around the leak, and the presence of metallic lead all point to the presence of metallic iron, which must have entered in the glass mix.

In the absence of iron, corrosion seems to be a combination of erosion and chemical action. This begins with the formation of superficial crevices, set up probably when the batch is thrown in. As the chemical processes of melting proceed and the gases are evolved, a boiling action develops together with a motion of the glass in currents which sweep over the sides and bottom of

the pot, these currents rising along the back and sides, which are much hotter than the bottom. This motion tears away portions of clay lining the crevices into which the glass has worked, giving rise in time to pitting or honeycombing, which is especially marked in the knuckle. The clay to a great extent passes into the glass or "dissolves," thus doing no harm, or rises to the surface as a scum which can be skimmed off. This is not true in other cases, where the clay remains in the glass as "stones," and the opaque particles are discovered in the finished ware. Solution of the clay in the glass results in the formation of feldspars, and, the glass being normally unsaturated with respect to alumina, the solution may proceed until the bottom of the pot is less than an inch thick, without actual leakage occurring in the worn area. "Stones" may be explained by assuming that the pot has been insufficiently heated in the bottom, which is in a soft-burned or "biscuit" state, and that erosion is very rapid, the fragments passing into the glass being so large that they cannot dissolve in the fining period, or that the glass dissolves some of the clay and then becomes saturated with respect to alumina. All available evidence shows conclusively that soft-burned, porous bottoms corrode excessively, while pots which have been burned to a dense structure offer great resistance to solution. This has been shown in the laboratory by melting a rather corrosive lead glass in 5-inch crucibles, a single melt sufficing to show marked or complete penetration of the bottom of the soft-burned crucibles, while the ones heated to a higher temperature showed a straight, white line of separation between the bottom and the glass. In the present work it was noted that all pots giving 5 melts or less were spongy and a light buff or cream color in the bottom. In fact, it is not possible under present conditions to burn the bottom in the arch to anything like the temperature needed to produce a dense, resistant structure. Travers¹ has shown that this difficulty may be overcome by allowing the pot to remain in the furnace at 1350° C for three days before filling, a solid wall being built up 9 inches in front of the pot, so as to ensure even heating. This practice would do much to remedy conditions in this country, though American glassmakers would undoubtedly object to the

¹ *J. Soc. Glass Tech.*, Sept., 1918, p. 171.

loss in production such a course would entail. With the idea of heating the bottom to a higher temperature, Jenkinson and Marson¹ have tried supporting the pot in the furnace on fire brick, but found that the bottom warped. At various times, glass-makers have tried burning the inner surface of the pot by introducing a gas- or oil-burner, but this practice was discontinued because it was impossible to spread the heat over a large area.

Sillimanite.—The formation of *sillimanite* ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) has been advanced by many investigators in explaining the resistance offered to corrosion by clay which has reached the "vitreous" stage. An exhaustive investigation of the formation of sillimanite and related minerals in glass pots and glass tanks has been made by Wilson,² who finds that, normally, sillimanite is developed only in the inner and outer *vitrified* surfaces of the pot, and not to any extent in the bottom. He also states that, with an aluminous clay, the boundary between the glass and the vitrified clay is very sharp, the hard clay surface being full of sillimanite needles, whereas a silicious clay is attacked in an uneven manner, the boundary being irregular and pitted. The life of the pot then depends on the rate of solution of the sillimanite layer; in the former case the glass adjacent to the pot is oversaturated with respect to alumina, whereas in the latter case it is unsaturated. The argument applies with equal force to tank blocks, particularly flux-line blocks. Since the heat inside a tank furnace is never sufficient to vitrify the blocks, it is imperative that all tank blocks be burned to a dense structure in the kiln. Travers³ points out very clearly that when the clay is vitrified merely by contact with the molten glass, the layer of sillimanite formed is exceedingly thin, whereas that formed in a thoroughly vitrified pot is rather thick. Corrosion in the former case is relatively rapid, especially in the bottom, which is not vitrified by the external heat. Consequently it is useless to vitrify a pot in the manner described above; moreover, it is doubtful whether much is to be gained by lining the pot with aluminous or similar material, because of the danger of such a lining cracking or wearing away in spots, exposing the porous inner clay.

¹ Jenkinson and Marson, *Loc. cit.*

² G. V. Wilson, *J. Soc. Glass Tech.*, Sept., 1918, p. 207.

³ *Loc. cit.*

Holes.—Concerning the remaining points enumerated above, only a few comments need be made. The question of holes developing in pots is an interesting but puzzling matter. It has been suggested that corrosion begins around a particle of iron (pyrite?), and the glass, having penetrated the surface, easily attacks the less resistant clay beneath. The trouble is one that at times crops up only in isolated cases, at times in a succession of pots, and is on the whole rather a mysterious matter. Of the 22 pots inspected, one had a hole through the side and one a hole through the back. The glass that escaped was clear, and there was no discoloration of the clay around the leak. On the other hand, of 4 pots developing cracks in the side or back, all showed traces of black glass. The theory that holes are due to metallic iron imbedded in the clay would be more impressive if discoloration and slagging of the clay beneath the hole could be detected in every case.

Deformation.—The question of softening and bulging of the pot in the furnace is always important, though, as previously stated, this defect is not usually serious, but occurs when the potmaker is forced, through inability to obtain a raw clay or deterioration of his regular bond clay, to experiment with new material and alter the proportions of raw clay to grog. Certain practices and conditions in glass works are productive of bulging: (1) failure to take down the stopper at the proper moment in the fining period, (2) "forcing" a pot in the hope of remedying stones, color or other defect in the glass, (3) excessive heating of a few pots due to uneven distribution of the heat within the furnace. As a means of judging the resistance to softening, the writer in both routine and experimental work has employed the warpage test, and has found it to be a direct and satisfactory method. The maximum temperature employed in this test was 2700°F. , rather than the lower figure of 2500°F. , which may be taken as the upper limit for the temperature of the glass. In the light of a previous discussion, it is probable that certain portions of the pot reach a temperature even higher than 2700°F. This surmise is based on the observed color and porosity of pieces taken from the crown and back wall of a number of pots. The porosity is found to increase in the direction of the bottom, which is always

very porous as compared with the "vitrified" portions further up. This condition is very bad, for it aggravates the natural tendency of the glass to corrode the bottom. To correct it, either of two courses may be followed: (1) to burn the bottom to an elevated temperature in the arch or furnace, or (2) to make the bottom of a mixture that becomes dense at a lower temperature.

The former alternative has received some consideration. In regard to the second course, from the writer's experiments and observations of pots recently in use, it appears that there is little to be gained by adding porcelain or similar feldspar mixtures to the pot clay, so long as the pre-heating is not sufficient to bring about a dense structure in the bottom. When pieces of such pots are examined, great fissures are seen extending everywhere through the mass, as though the dense, whitish grains of porcelain had shrunk away from the more refractory matrix. This condition is due to the fact that the different materials were not intimately blended, and is unavoidable when the porcelain is introduced as grog. However, the writer has found that this segregation of the porcelain in the form of white grains occurs even when the raw kaolin, feldspar and flint are individually ground very fine and thoroughly blended with the fire clay. Where such a mixture is in contact with the glass, vitrification extends no further than a depth of about a millimeter, and is not sufficient protection against corrosion because of the rapid solution of the vitrified layer and the danger of a crack exposing the porous material of the interior. Bleininger¹ has recently shown that the porcelain optical glass pot may corrode as much or more than an ordinary pot unless it has been heated to at least 1400° C before introduction of the glass batch.

If the bottom alone were made of a different, denser-burning mixture, trouble would arise from the difference in shrinkage between the bottom and walls, and the possibility of cracking at the knuckle. The fact that bottom-clay is worked stiffer than side-clay would tend to obviate the former, but increase the latter difficulty. Under present working conditions, the walls must not be made less refractory, rather the contrary; moreover, if the pot were as a whole more refractory than it is now, special glasses

¹ *J. Am. Ceram. Soc.*, 1918, p. 21.

requiring a more elevated working temperature could be melted. All things considered, it is to be hoped that experiments on the use of more refractory substances than fire clays as basic materials in pot construction may be carried out by the intelligent coöperation of pot manufacturers and glassmakers, and that such attempts will lead to gratifying results.

Summary.

1. Examination of the remains of pots used in melting lead glass shows that cracking and corrosion are the chief causes of failure.

2. Cracks are due to strains set up by (1) too rapid heating in the pot arch, (2) insufficient pre-heating, (3) by throwing in the glass batch. The second cause is perhaps the most serious source of trouble.

3. Corrosion is due in some cases to the slagging action of iron on the clay, in most cases to solution of the clay in the fusing alkalies and molten glass. Solution of the clay tends to color the glass, owing to the iron content of the clay, but the tint can be neutralized. Black glass and metallic lead found in pot bottoms are considered to be due to metallic iron in the glass mix.

4. Inability to burn the bottom of the pot in the pot arch accounts for the rapid corrosion of the clay. The trouble might be remedied by allowing the pot to remain empty in the furnace for three days, but glassmakers would object to the loss of production entailed.

5. The vitreous layer formed by heating the inner surface of the pot with an oil-burner, or by the molten glass itself, is very thin, and is not sufficient protection against the attack of the glass. Lining the pot with aluminous or porcelain-like material will not help if there is danger of the lining cracking away (in drying or burning) and exposing the more porous pot clay beneath. The safer method is to burn the pot thoroughly at a temperature of 2500° F., the heat being applied *directly* to the bottom.

6. It appears that little is to be gained by adding porcelain as grog to the pot batch, unless the mixture is rendered dense before use. Moreover, this procedure is objectionable because it would increase the tendency of the walls to bulge.

7. In view of the difficulties attendant upon the use of one clay for the bottom and another for the walls, it seems desirable to search for some material superior to fire clay in refractoriness and in resistance to corrosion.

In conclusion, the writer desires to thank Messrs. Jones, Hess, Barry and Nipper of the Libbey Glass Co. for their kind aid and many valuable suggestions.

CERAMIC LABORATORY,
THE BUCKEYE CLAY POT CO.,
TOLEDO, OHIO.

AN UNUSUAL CAUSE OF SPALLING OF SEWER PIPE.

BY CULLEN W. PARMELEE.

Not long ago the writer was requested to investigate the cause of spalling of sewer pipe which occurred during the burning of the ware. The pipe as it came from the kiln was marred by the flaking of the outside surfaces. Usually these flakes were detached. Sometimes they were almost but not quite separated from the pipe. An examination of the ware showed that in practically every instance a small fragment of what had been a more or less spherical hollow body was imbedded in the detached spall and the other portion of the spheroid was attached to the surface of the fracture of the pipe. These spheroids were about 2 to 3 mm. in diameter. Under a magnifying glass they showed the characteristic appearance of small geodes, that is, small hollow bodies with the interior face of the cavity lined with small crystals. Our opinion regarding the nature of these spheroids was confirmed by members of the faculty of the Department of Geology.

The occurrence of geodes in clay is probably rather unusual but they are known to occur in certain clay deposits in Illinois, notably in the vicinity of Hamilton. These geodes, we are informed by one familiar with that locality, vary in size from a marble to those which are six inches or more in diameter. The larger are more commonly found and do not give rise to trouble except for the expense of repairs to the machinery—due to breakage if these hard nodules are not first removed from the clay.

The spalling, which we observed, accompanied the use of a clay which is of a different character and geological occurrence from that at Hamilton. At the latter place, the geodes are of common occurrence while at the other locality their presence was not known previous to our investigation.

After having determined the probable cause of the trouble, we undertook to locate the stratum containing these nodules. A search of the floor of the clay pit was rewarded by the discovery of a geode imbedded in a large block of a sandstone conglomerate,

which originally had formed part of the rock mass underlying the clay deposit. A painstakingly thorough examination of the rock ledge resulted in the discovery of a number of small geodes varying in size from a hickory nut to a large bean. Together with these geodes was found a remarkable accumulation of more or less perfect quartz crystals, double ended, each not much larger than a kernel of rice. These geodes apparently were located in a very small area on top of the sandstone underlying the clay deposit.

The spalling occurs, apparently, during an early stage of the burning. This is indicated by the small cracks on the reverse side of each spall and radiating from a point almost exactly above the geode fragment—showing that a strain was developed while the clay was at a temperature too low to have given it a permanent set.

The small geodes which we found were all lined with quartz crystals. We are uncertain as to whether the spalling was due to the popping of the geodes—due to the expansion of the air-filled cavities—or whether it was due to the expansion of the quartz particles. Probably the former was the cause.

DEPARTMENT OF CERAMIC ENGINEERING,
UNIVERSITY OF ILLINOIS.

ACTIVITIES OF THE SOCIETY.

January 4, 1918.

Annual Meeting.

Plans are being rapidly formulated for the Annual Meeting, which is to be held in Pittsburgh on February 3, 4, and 5. This will be the twentieth anniversary of the formal organization of the Society, and preparations are being made to commemorate the occasion in fitting manner. Among other things being planned are a banquet, the elevation of a large group of associate members to active membership, the election to life membership of some of the men active in the organization and early development of the Society, and the conferring of Honorary Membership on one or more men whose services in the advancement of ceramic technology has been especially noteworthy. Arrangements are being made to have representatives of allied scientific and technical societies take part in the anniversary program.

This meeting will be of special interest also from the standpoint of the technical and practical worth of the papers and discussions. The forming of Professional Divisions is arousing great interest among the manufacturers and plant executives of the various industries represented on our membership rolls. Papers of interest and practical value to each of these groups are being prepared and arrangements have been made to have these read and discussed in separate sessions of the Professional Divisions. This will give opportunity for free discussion and interchange of views by the men actively engaged in the particular industry represented by the Division. More papers of the kind indicated are earnestly solicited.

A joint session with the United States Potters' Association, many of whose members are also members of our Society, is being arranged. During the same week, annual meetings will be held in Pittsburgh by the National Brick Manufacturers' Association, the National Paving Brick Manufacturers' Association, the National Building Brick Bureau and the National Clay Machinery

Manufacturers' Association. Opportunity will be given for inspection of the laboratories of the Bureau of Standards and Mellon Institute as well as the unparalleled variety of ceramic plants in the Pittsburgh district.

At the business session several matters of vital importance in the management and development of the Society will come up for decision.

Make your plans now to attend the meeting. It will be the largest, most important, and most enjoyable meeting ever held by the Society. You cannot afford to miss it.

Professional Divisions.

In accord with the motion of Mr. Montgomery reported in Number 8 of the Journal and recently adopted by the Board of Trustees, the President has appointed the following members to act as organization leaders of Professional Divisions.

White-ware and Porcelain.....	C. L. Sebring
Refractories.....	A. V. Bleininger
Glass Technology.....	C. H. Kerr
Abrasives.....	R. C. Purdy
Enameled Metals.....	R. D. Landrum
Terra Cotta and Faience.....	F. B. Ortman
Brick and Tile.....	M. P. Blair

Members are urgently requested not to wait for an appeal from the leaders, but to become actively interested themselves and to arouse the interest of every ceramic man they know in the organization of one of these Divisions.

Nominations for Active Membership.

The Board of Trustees desires that members send to any member of the Board at once nominations for active membership. Many of our associate members deserve this elevation, and it is desirable that the voting power in the Society be more widely distributed. It is to be noted that the presentation of papers is no longer the sole basis for elevation to active membership. Following are extracts from the revised rules of the Society covering this subject:

"Active members must be persons competent to fill responsible positions in ceramics. Only associate members shall be eligible to election as active

members and such elections shall occur only in recognition of attainments or of service in the science, technology, or art, of the silicate industries."

"To be promoted to active membership associate members must be nominated in writing by an active member, seconded by not less than two other active members, and approved by the Board of Trustees. Their nomination must be accompanied by a statement of their qualifications and to be elected they must receive an affirmative vote of the majority of the members of the Board of Trustees."

Honorary Secretaryship.

DECEMBER 22, 1918.

MR. HOMER F. STALEY,
Bureau of Standards,
Washington, D. C.

MY DEAR STALEY:

I am in receipt of your message to the effect that the American Ceramic Society desires to create a new office, that of Honorary Secretary, and to elect me to it. I am, of course, not insensible to the honor which the Society desires to confer upon me, and greatly value this added proof of their good will. Nevertheless, I must refuse it.

The custom of having Honorary officers is common and well established in English and European Societies, but here it is rather anomalous. In England, the Honorary officers have little part in the actual achievements of the organization, the work being done by the active officers, but the position fills a useful purpose nevertheless, as there are always members of the upper class whom it is desirable to recognize.

I should be loath to see this custom, which belongs to a social structure quite different from ours, become popular in the United States, and still more unwilling to see myself figuring in such a capacity. When the exigencies of the war are ended, if I find that I can take up the threads of my former life again, the only status I should care to have in the Society would be that of an active worker, where I could mingle on terms of exact equality with everybody, and where I would be unhampered in making any views and purposes felt.

I feel sure that you can make the Society see, after they have given the matter a little more deliberate consideration, that the course which I propose is really the safe and democratic one and is for their best interests.

With kindest personal regards,

(Signed) EDWARD ORTON, JR.,

LIEUT.-COLONEL, M. T. C.,
UNITED STATES ARMY.

JOURNAL

OF THE

AMERICAN CERAMIC SOCIETY

A monthly journal devoted to the arts and sciences related to the silicate industries.

Vol. 1

October, 1918

No. 10

EDITORIALS.

IMPORTED CLAYS.

With the signing of the armistice there appeared to be a cessation of the agitation of many months past in reference to the importation of the clays of different kinds. Undoubtedly with the closing of hostilities many of our manufacturers began to look with longing eyes to a fresh and adequate supply of the imported materials, especially those used in the manufacture of the white burning pottery products. Nor were they doomed to disappointment as we have already learned of an increased flow of the imported clays.

That the efforts of our geologists and laboratories have not been fully rewarded in the location and development of new and adequate deposits of white burning clays of first quality is to be regretted. Let us hope that there will be no let-up in their efforts and that the field and laboratory searches will be continued.

Doubtless the situation as regards the importation of clays for crucible, pencil and glass pot manufacture will remain the same for some time to come. American clays in glass pot mixtures appear to be giving very good satisfaction and the production of clays for this purpose appears to be on a well established basis. The results secured with American clays in graphite crucibles are showing steady improvement, and it is to be hoped that our crucible manufacturers will never again be dependent upon the foreign deposits for this highly important commodity in their industry.

THE POTTERY INDUSTRY.

When viewed as a whole, there has not been a marked change in the quality and general nature of the pottery wares manufactured in this country during the years of the war. It is true that we have long excelled in the quality of certain of our pottery manufactured products, especially of a structural nature such as electrical porcelain, sanitary ware, etc. In a general way, however, the bulk of our wares is of the same quality as before the war.

Our pottery manufacturers still cling to the use of ball clays. True, the elimination of ball clays from body mixtures involves more or less radical changes in methods of molding, burning temperatures, etc. So long as the ball clays are used, however, it will not be possible to produce wares which compare favorably in color and cleanliness with the hard porcelains of Continental Europe. We do produce in limited quantities wares which are not inferior in appearance and quality to the best of the imported wares. Our wares of this kind, however, must be classed as art wares and cannot compete in price with the bulk of the table wares which were imported in large quantities previous to the war and sold at amazingly low prices in competition with the American-made pottery.

Will our manufacturers be satisfied to return to the former conditions of competition or will their efforts to raise the standard of quality be stimulated? It is to be hoped that the technique of this branch of the pottery industry will keep pace with the advancement made in some of the smaller and less important branches.

ORIGINAL PAPERS AND DISCUSSIONS.

A DISCUSSION OF TERRA COTTA DRYERS.

By ELLIS LOVEJOY, E.M., Columbus, O.

As we recall the various terra cotta dryers we have examined and designed, the thought comes to us that the manufacturers of terra cotta have not come to any system in dryers; that the dryers used differ widely in character and efficiency; that the ware, built up from several clays and grog, will stand severe treatment in the simple shapes and only the large and complicated shapes require more careful treatment; and finally that increasing competition will require the manufacturers to adopt more economical methods of drying and burning.

There are in use several ordinary waste-heat car tunnel progressive dryers. The waste heat progressive dryer holds a prominent place in the clay industries. It uses the heat of cooling kilns and that of engine exhaust, and, in consequence, it is economical in fuel. The dryer conditions seem to be ideal. The ware enters a humid low temperature atmosphere, and as it advances, the humidity decreases and the temperature increases, until finally near the exit it is subjected to upward blasts of hot air through the floor ports. It is desirable in the manufacture of terra cotta that each lot of ware come through about the same time and where there are a number of tunnels this condition is fairly well met. The operation of the dryer is not so ideal as it would appear. As long as the operation is continuous the conditions in the tunnels are constant, but continuous operation is not customary. There is a forward movement of the heat and a drop in humidity in the tunnels during the night when the ware is not moving, and a corresponding retreat in the daytime when the tunnels are

being emptied and filled. This variation in the tunnel conditions may be withstood by the margin of safety in the drying behavior of the ware. The tunnel conditions vary much more widely over holidays and some wares may not stand this variation, but stopping the fans during all or part of the period may give sufficient control. Thus far, however, the progressive tunnel may be said to meet the requirements.

There is a more serious objection. It is impractical to so load the cars with terra cotta as to closely fit the tunnels. Almost invariably there is excessive space between the tunnel roof and the top of the ware and the air rises into this space. Since the air movement beyond the hot air zone in the tunnel is horizontal, the top of the ware, or the top ware, is subjected to maximum drying conditions while very little drying progress occurs in the bottom. When the cars reach the hot zone the bottom green ware is subjected to the severe conditions imposed by the blasts of hot air coming through the air ports and it is to this ware in this zone that great damage is likely to occur. It is readily seen that the top ware is safe in the hot zone because of its advanced condition and its position relative to the air blasts. It frequently happens that the top ware is damaged in the early stages near the receiving end and this is often attributed to a lack of humidity, but it is our opinion that it is more often due to unequal drying.

The users and advocates of the progressive tunnel may say that the ware readily withstands these conditions and that the dryer is satisfactory. We wonder how far this is true. If there is no loss in either dryer or kiln there can be no question in regard to the efficiency of the dryer and the operators are to be congratulated on the strength of the body which they have developed, but this is not conclusive, and one is not warranted in adopting such a dryer as the best for the product in general. In other lines of ware we have too frequently seen the weakness of the progressive dryer to be convinced that it is the best type for the manufacture of terra cotta.

In drying other wares we have found a decided improvement both in the rate of drying and in the per cent of perfect output by extending the hot air duct nearly or quite the full length of the tunnel and thus securing up-draft through all the ware. At first

glance this seems more severe than the original type, and on the whole it may be so, but the ware is subjected to more uniform conditions. The temperature of the air is lowered by wall and ground absorption as it advances in the lower duct, and with graduated floor slots the conditions at the car receiving end may be materially less severe than at the delivery end. We still have the forward movement of air in the tunnels with increasing humidity, and there will be decidedly more circulation in consequence of the upward currents into the horizontal current. We have seen terra cotta regularly subjected to decidedly more severe treatment, and while this ware may have been exceptional in its drying behavior, yet the fact that it is a prepared body heavily grogged leads us to believe that it will generally stand more severe drying tests than many of the common wares made from a single clay.

The chief weakness of the usual progressive tunnel is lack of circulation. We dry and harden the top ware without getting drying conditions down into the mass of ware. If the ware will stand the direct up-draft heat the full length of the tunnel as above suggested, an economical dryer for terra cotta is a simple problem, but if not then we must improve the operation of our present type by better circulation, or in other words, break up the horizontal current of air in the top of the tunnel and drive it down among the ware.

The value of circulation is remarkably demonstrated in recent dryers nor is the idea new.

It seems to us that in the progressive dryer, the operation could be in two stages. Make the delivery (hot) end as in the usual progressive tunnel, then midway, or less than midway, of the tunnels put a cross duct on top of the tunnels, similar to the under-ground hot-air duct at the delivery end, with an opening through the bottom of this duct (tunnel roof) into each tunnel. Draw the air from the tunnels by means of a fan and return it to the tunnels through a second cross duct and lateral ducts on top of the several tunnels. In other words, duplicate on top of the tunnels from the center to the receiving end, the duct system at the delivery end, except that the air for the receiving end would be drawn from the tunnels themselves instead of from

cooling kilns or through steam coils. The partially to nearly dry ware in the delivery end will be subjected to *upward* blasts of hot dry air. From the center to the receiving end the green ware will be subjected to *downward* blasts of lower temperature higher humidity air in which the temperature decreases and the humidity increases toward the end. In such a construction we retain all the ideal features of the progressive tunnel and overcome the very serious horizontal over-draft difficulty without any increase in fan equipment of the modern two-fan dryer.

A progressive tunnel equipped with steam coils only and making no use of waste kiln heat is, or soon will be, economically out of the question. In our opinion the most essential economy in the future of the business is the use of the heat from the cooling kilns for drying even though the future factory makes use of the continuous or car tunnel kiln.

The box systems in use in several factories, it seems to us, are far from satisfactory and are not economical. The ware is set in a closed room. Blasts of air are turned into the room and, by one means or another, directed to an exit. The treatment is severe, and the heat waste excessive. The air volume and consequent heat supply is practically constant, while the moisture removed passes from a maximum to virtually zero. At the end of the drying we are heating a large volume of air and forcing it through the dryer without any return whatever. A better operation is to return the air to the fan, replacing some loss with fresh air. Thus we get the humidity conditions and at the same time conserve the heat. The usual equipment is the steam coil with exhaust steam in the day and live steam at night. So far as we know, waste heat from cooling kilns is not used, perhaps because of the greater ease in regulation of the temperature and also because the profits of the business have not insisted on economies. The introduction of kiln heat into a factory building not fire-proof involves a questionable fire risk although a number of sewer pipe factories have made such use of it.

The humidity treatment is nicely carried out in the regenerative type of tunnel dryer. The tunnel is two storied. In the upper tunnel, or duct, are steam coils, with a fan at one end. The lower tunnel is filled with cars of ware. The two tunnels are connected

at each end. When the cars are placed, the doors closed and the fan started, the fan picks up the air from the lower tunnel, drives it through the coils to the opposite end of the upper tunnel, then down into the lower tunnel and back among the ware in the lower tunnel to the fan. Thus we have a complete cycle repeating ad libitum. It is necessary, of course, to provide a vent for the escape of some of the saturated air and replace it with fresh air through an inlet to the fan, and this may be extended to the extent that all the intake air is from the outside without any regeneration. The number of such dryers is too limited to draw any conclusion. It is in a class with the regenerator box dryers with the handicap of multiple fans and horizontal air movement. Steam supplies the heat, and live steam so far as we know, but there is no reason why exhaust steam may not be used. It is not practical to use waste kiln heat in connection with regeneration and natural humidity except by the use of an economizer equipment which would be expensive in initial installation and maintenance. There is, however, an excess of waste kiln heat and no occasion for regeneration except to get natural humidity. Humidity could be obtained in other ways than from the ware, but it requires regulation and risk not involved in the natural operation. It is inconceivable, especially if the tunnels are short, that moisture taken from the ware in exchange for heat could saturate the air to the extent of the dew point, whereas careless artificial humidation might easily saturate in excess of the dew point and result in considerable damage to the ware.

We have in this regenerative tunnel dryer the same difficulty of horizontal air movement over the top of the ware without satisfactory circulation around the ware as in the progressive car tunnel and in greater degree in that there is no upward movement as in the delivery end of the progressive tunnel. The horizontal movement can be broken up by a duct between the upper heating tunnel and the lower drying tunnel, with ports into the latter. Thus the air from the upper heating tunnel would return through this delivery duct and be blown down, on the ware, through the graduated ports in the under side of the return duct. As stated above, we do not believe that the air naturally could be saturated to excess in the original construction, but should it be possible,

the use of the return duct delivering hot air at intervals from end to end of the tunnel would greatly lessen the possibility.

The return duct could be eliminated and graduated ports be placed in the division floor between the two tunnels and thus simplify the construction, provided the steam coils are at one end of the upper tunnel.

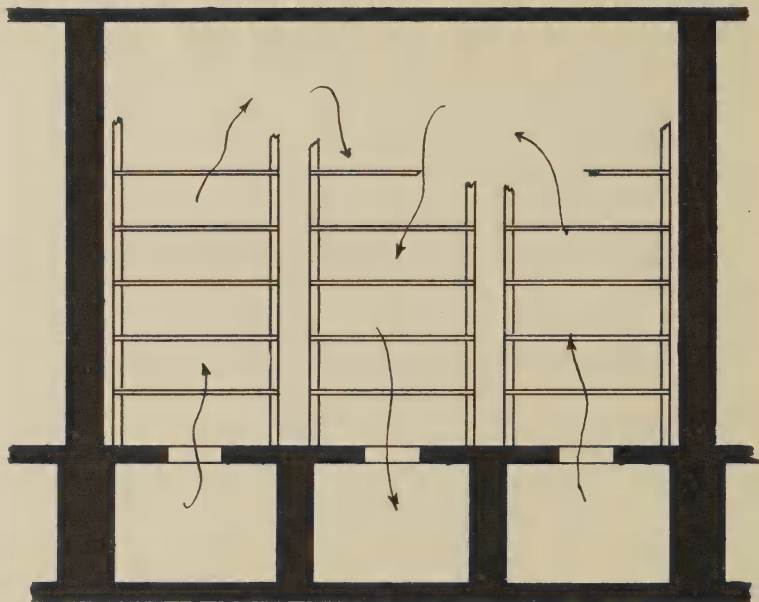


FIG. 1.

Another idea would be to place the return duct under the lower tunnel floor and blow the air upward among the ware, thence horizontally to the end of the tunnel and into the fan, but this involves an awkward connection between the heat tunnel and delivery duct.

The only advantage that we can see in the double tunnel in its original form over the usual progressive tunnel is that it may be limited in length and thus better adapt itself to many factory layouts, and in that the humidity conditions are probably more satisfactory. Its fuel cost in live steam and multiplicity of fans give a balance in favor of the progressive waste heat tunnel.

A recent innovation in tunnel dryers, not as yet, however, applied to terra cotta, has a wide tunnel with three under-floor ducts as shown in the sketch. (Fig. 1.) The two outside ducts supply the hot air from the cooling kiln and the central duct is the exhaust. The hot air rises among the ware on pallets over the side ducts and passes down among the ware over the central duct. The central duct could be used for hot air and the side ducts for exhaust or two ducts could be used instead of three,—one for hot air and one for exhaust. If all the ware will stand the direct heat, that slowest in drying could be placed over the hot air ducts and the quick drying ware over the exhaust duct. Since the outgoing air would have greater humidity than the incoming air, the ware over the exhaust would be retarded in its drying. Another view would be to place the safe drying ware over the hot air ducts and the difficultly drying ware over the exhaust duct. This would require a longer drying period but insures greater safety, and in some degree gives humidity for the more difficult ware. If a more complete humidity operation were required, the moisture would have to be introduced into the incoming hot air and reduced as the drying progressed.

One's first thought would be the possibility of short circuiting from the hot air ducts to the exhaust duct, but this would be easily overcome with the foot-pallets in use in a number of factories. The tunnels would be roomy and satisfactory for motor trucks. The danger of short circuits with cars would be greatly increased, and it probably would be necessary to have a curtain wall between the cars which would insure the full up- and down-movement. The feature of the dryer is the circulation, and there are no restrictions in regard to length, except that excessive length decreases the chances of getting uniform exhaust from end to end. This problem is less difficult and more easily solved in a dryer than in rectangular kilns where we have in some installations end-draft up to ninety feet in length.

Floor drying as in sewer pipe factories, with covers to get humidity, increases the floor space required, heats the working space unduly and increases the humidity therein, and finally requires live steam in a large measure. It has the advantage that the ware can be watched and the drying of individual pieces controlled,

but the manufacture of terra cotta is no longer the modeling of lions rampant and recumbent, of decorative friezes and capitals. The bulk of the ware is in small pieces duplicated indefinitely and the need of an independent dryer to take the ware from the floor is imperative.

Ducts from the kilns or boilers under the pressing floors are in use but in our opinion are questionable, and blowing hot air into the press room at night from kilns or steam coils is not a satisfactory drying system. "Better working conditions" are the basis of many labor disputes and often times justly so, and factory operations must meet these conditions. Where it is necessary to hold the ware on the floor until it is fully set (leather hard) it would be better to provide a steam heated slatted floor for this preliminary drying, or in case it is not desirable to move the ware at all, then after filling one section of the floor, move the pressmen to another section and turn steam into the pipes under the first section, or use steam only at night. It is not our purpose to discuss sanitary factory conditions which have no bearing on subsequent drying, except as the factory is the dryer. We are of the opinion that a properly developed independent dryer with suitable control will eliminate much of the hot floor press room drying.

The wide divergence in dryer types indicates that terra cotta manufacturers have not solved the dryer problem.

The essentials are waste-heat, thorough circulation and controllable humidity. We do not know of any dryer which includes all of these. In some instances humidity is of less importance. This leaves waste-heat and circulation to be combined, yet simple as the problem is, we have not seen the solution of it in operation in any terra cotta factory.

THE COMPOSITION OF CHINESE CELADON POTTERY.

By J. S. LAIRD.

The raw materials used in the modern ceramic industry in China, together with the compositions of the bodies, glazes, and colors employed, have been studied very thoroughly by the ceramists of the Sèvres potteries, Ebelman and Salvétat,¹ in 1850, and Vogt² in 1890. The latter investigator has confirmed his results by preparing from European materials bodies exactly corresponding to the Chinese, and has reproduced many of the famous glazes, including crackle ware and flamed red or sang-de-boeuf.

Our knowledge of old Chinese pottery is much less complete. Very few specimens have been examined scientifically as their value as works of art and antiques has discouraged the destruction incidental to chemical analysis. In the hope of obtaining valuable data on this subject an examination of the sites of the ancient kilns at King-to-chen was undertaken a few years ago by Mr. Charles L. Freer of Detroit, the well known collector and authority on Chinese pottery. Internal troubles in China have up to this time made excavation of the kiln sites impossible. Two interesting specimens were, however, obtained and examined analytically. These partial results are reported in this article.

Specimen 1.—This specimen consisted of a lump of glaze which had dripped off the ware in firing and solidified on the kiln floor. While it was undoubtedly old, its exact date has not been fixed. It was a solid, homogeneous lump, in color bluish green or "celadon" with reddish streaks. Where it had hardened on the kiln floor it had picked up particles of sand. These particles were carefully ground off the sample taken for analysis.

Specimen 2.—The second specimen obtained was a small plate or saucer about five inches in diameter. It probably belonged to the Yuan period and showed its antiquity by a marked weathering. The body of this plate was fairly dense and fine grained,

¹ Ebelman and Salvétat, *Ann. chim. phys.*, 313, 257.

² Vogt, *Bull. soc. encour.*, 99, 530.

but soft enough to be easily scratched by a knife. It was light colored, inclined to buff with reddish streaks. Its composition and appearance would class it as a fire clay and not a kaolinitic body.

All but the foot of this plate was covered with a thick opalescent bluish green glaze showing a small uniform crazing. It was sufficiently opaque to completely hide the body of the ware. A blotch, shading in color through bright red and green to black, marked a spot where apparently a cinder had fallen on the ware during the firing. Sufficient of the glaze for analysis was removed by careful chipping with a small chisel, and thanks to the thickness of the glaze it was possible to obtain a sample entirely uncontaminated by fragments of the body. It was not possible to obtain separate samples of the red or green portions.

The analyses of these two glazes and of the body of the plate are given in Table 1.

TABLE 1.

	Glaze 1 (lump).	Glaze 2 (plate).	Body (plate).
SiO ₂	72.52 per cent	66.40 per cent	63.20 per cent
Al ₂ O ₃	10.59	13.88	28.30
Fe ₂ O ₃	0.41	0.30	3.47
FeO.....	2.02	1.19	...
CaO.....	8.48	11.58	2.05
MgO.....	1.24	1.61	trace
K ₂ O.....	3.77	4.25	1.98
Na ₂ O.....	1.48	1.84	0.37
MnO.....	trace	trace	trace
TiO ₂	trace	trace	trace
P ₂ O ₅	0.21	..	trace
	100.72	101.05	99.37

Except for the presence of iron, these glazes are closely related to the cone 4 type of whiteware glazes and are quite calcareous, No. 2 being even higher in CaO + MgO than the cone 4 formula.

Color of the Glazes.—It will be noted that the only coloring oxides present in the glazes in appreciable amounts are oxides of iron, particularly ferrous oxide. The presence of the oxides commonly employed to give blue or green colors—copper, cobalt and chromium—could not be detected by the most careful tests. When

particles of these glazes were remelted in an oxidizing atmosphere they became almost colorless. Vogt¹ found that the blue-green color of modern celadon glazes was developed only when the ware was fired in a strongly reducing atmosphere, otherwise a pale yellow was produced. Compounds of ferrous iron must therefore have given the color of these glazes, the peculiar opalescence being due probably to the high percentages of lime and alumina.

Comparison with Other Reports of Celadon Glazes.—Meyer² has reported analyses of the body and glaze of an old celadon vase brought from China, and Ebelman and Salvétat³ and Vogt⁴ analyzed modern celadon glazes and the bodies on which they

TABLE 2.
Chinese bodies used with colored (celadon) glazes.

Ware. Analyst.	1. Yuan. Laird.	2. Old Chinese. Meyer.	3. 1850. Salvetat-Ebelman.	4. 1890. Vogt.
SiO ₂	63.20	69.51	69.0	69.50
Al ₂ O ₃	28.30	22.72	23.6	23.10
Fe ₂ O ₃	3.47	1.84	1.2	2.00
CaO.....	2.05	0.27	0.3	0.16
MgO.....	trace	0.36	0.2	0.22
K ₂ O.....	1.98	4.79	3.3	3.72
Na ₂ O.....	0.37	0.87	2.9	1.12
	99.37	100.36	100.5	99.82
Celadon glazes used on these bodies.				
SiO ₂	66.40	64.98	72.00	70.2
Al ₂ O ₃	13.88	14.33	6.00	14.8
Fe ₂ O ₃	0.30	1.39	2.50	1.5
FeO.....	1.19
CaO.....	11.58	10.09	10.40	8.1
MgO.....	1.61	1.55	trace	0.2
K ₂ O.....	4.25	5.61	9.10	3.2
Na ₂ O.....	1.84	0.81		2.1
TiO ₂	trace	1.39	trace	trace
MnO.....	trace	trace	trace	trace
	101.05	99.15	100.00	100.1

¹ Vogt, *Loc. cit.*

² Meyer, "Der Alter Seladon Porzellan," 1885.

³ Ebelman and Salvétat, 3rd Memoir.

⁴ Vogt, *Loc. cit.*, p. 562.

were used. According to the latter, the body was prepared from an impure dark-burning kaolin softened by the addition of micaceous pegmatite. The glaze was a combination of the pegmatite with iron-bearing clay and milk of lime, the lime having been ignited several times with fern fronds. This corresponds with the description given by Pere d'Entrecelles two hundred years ago in the first reports sent to Europe of the ceramic art in China.

These analyses are combined with the analyses of this piece of very old Chinese pottery in Table 2. The analyses are quoted from the article by Vogt as the original papers are not available.

From the higher percentages of iron, lime, and alumina, and lower percentages of alkalies, it would seem probable that a natural clay and not a modified kaolin had been used in the body of the Yuan pottery. Ferrous iron is not reported in any of the other analyses, probably because no attempt was made to determine the state of oxidation of the iron present. Otherwise the composition of the two oldest glazes are quite similar, and do not differ greatly from the most modern. It is quite interesting that without the aid of accurate methods of analysis, in fact, depending in their selection of material largely on visual inspection, the Chinese potters have controlled the composition of their glazes within very narrow limits over a period of probably ten centuries.

UNIVERSITY OF MICHIGAN,
ANN ARBOR, MICH.,
December 14, 1918.

THE HYDRAULIC PROPERTIES OF THE CALCIUM ALUMINATES.¹

BY P. H. BATES, Pittsburgh, Pa.

Introduction.

The Pittsburgh Branch of the Bureau of Standards has been conducting several investigations dealing with the hydraulic properties of all of the compounds in the lime-alumina-silica system. These have been carried on in connection with a general investigation of portland cement. It will be recalled that the compounds of this system are:

CaO.SiO_2	$3\text{CaO.Al}_2\text{O}_3$	$\text{Al}_2\text{O}_3.\text{SiO}_2$	$\text{CaO.Al}_2\text{O}_3.2\text{SiO}_2$
$3\text{CaO}.2\text{SiO}_2$	$5\text{CaO}.3\text{Al}_2\text{O}_3$		$2\text{CaO.Al}_2\text{O}_3.\text{SiO}_2$
2CaO.SiO_2	$\text{CaO.Al}_2\text{O}_3$		$3\text{CaO.Al}_2\text{O}_3.\text{SiO}_2$
3CaO.SiO_2	$3\text{CaO}.5\text{Al}_2\text{O}_3$		

Some of these exist in several forms, notably the dicalcium silicate or orthosilicate, which can exist in four—depending upon the manner in which it is melted or the temperature from which it is cooled.²

Such an investigation should be of considerable interest and should furthermore be carried on in connection with a similar one dealing with portland cement, because, while it does contain materials other than lime, alumina or silica, these form ninety per cent or more of this important structural material. At the same time, the limits within which its composition may vary cover but a small part of the total area of the ternary system. This restricted composition of portland cement is the result of evolution, that is, it has been found by years of trial that a cement of about the average composition of commercial brands can be more economically made and gives better results

¹ By permission of the Director, Bureau of Standards. Read at the December, 1918 meeting of the Pittsburgh Section of the American Ceramic Society.

² Rankin, "The Ternary System Lime-Alumina-Silica," *Am. J. Science*, 39, Jan., 1915.

in application than others having materially different compositions. Thus the natural cements, containing frequently very high amounts of magnesia or widely varying amounts of silica or alumina, could be produced more cheaply but require longer periods of hardening in order to develop strength equivalent to that of the portland cements. Under certain conditions slags also develop slowly but ultimately very satisfactory hydraulic properties. But even the area embraced by the compositions of these three materials (portland and natural cements and slags) covers but a small part of the area of the system. Therefore, the entire system offers fields for exploration to see if any other portions of it contain compounds which under the action of water possess the property of hardening either in air or water, and whether after such hardening they remain either weather-resisting or are able to resist the further action of water. These two properties, especially the latter, constitute "hydraulic properties."

While it has not been possible to produce all of the compounds of the system in the desired amounts and purity, the entire system has been covered by burnings on batches having compositions very similar to those of all of the different compounds. It was found that the following alone developed hydraulic properties: $2\text{CaO} \cdot \text{SiO}_2$ (β -form); $3\text{CaO} \cdot \text{SiO}_2$; and all of the aluminates except the tricalcium aluminate. The fact that the tricalcium aluminate, the only aluminate present in portland cement of normal composition and burning, does not have the desired hydraulic properties is very striking. At the same time one is impressed just as much by the fact that the other aluminates of lime all have this property of hardening and acquiring at early periods strengths in excess of those acquired by portland cement at the end of an equal period. The aluminates are, therefore, worthy of especial consideration and the remainder of this paper will be given over to a brief discussion of their production, their properties, and the chemistry of their hardening.



The tricalcium aluminate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3$) can be prepared in a pure condition with some difficulty. It decomposes at about

1535° C into CaO and liquid. If this decomposed material is reground and reburned at a temperature of about 1350° C for several hours, it is possible to secure the aluminate free from any CaO. This ground pure tricalcium aluminate, on the addition of water, agglomerates into masses, the exteriors of which alone are hydrated. At the same time there is a vigorous evolution of heat—the mass giving off steam copiously. By grinding in a mortar it is possible to secure a fairly smooth paste free from a great amount of the hard agglomerated granules of the material which have not been acted upon.

If pats of this paste are placed in a damp closet, they seem to acquire both an initial set (in about three hours) and a final set (in from 48 to 72 hours). But if the interiors of the pats are examined they will be found to be quite soft, and frequently, if they are allowed to remain in a damp closet for about a week, they become very soft throughout. If placed in water they disintegrate completely. The product of hydration is hydrated tricalcium aluminate, which is at first in a colloidal (gelatinous) form but is rapidly converted into a crystalline form.

The question naturally arises—does this tricalcium aluminate act in a similar manner in normal portland cement? If so, what masks or retards this action—which apparently does not take place when cement is gaged with water? If it does not, what is there in the cement which so modifies the properties of the tricalcium aluminate so that it appears to have hydraulic properties?

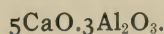
Before considering these questions, it is well to remember that alumina (Al_2O_3) is not required in portland cement—except to make it possible to produce it on a commercial scale. A cement having all of the properties of portland cement and containing less than one-half of one per cent of alumina can be produced. A cement of this kind, however, cannot be produced in a rotary kiln or at a temperature which would make its production a commercially feasible proposition. In the manufacture of portland cement the presence of alumina is necessary to the lowering of the temperature of burning to such a degree that a ternary system may be formed (without too great an expenditure of heat) and from which the tricalcium silicate—the active hardening constituent—may separate.

If a section of portland cement clinker is examined it will be noticed that the constituents do not have a well-defined outline nor are they separated into well-defined crystals. The dicalcium silicate—the major constituent—exists in fairly large grains which blend off into a more or less homogeneous boundary containing the tricalcium aluminate and tricalcium silicate as a bonding material. Although in a well-burned clinker having a high silica content the tricalcium silicate does exist in well-defined crystals, it should be remembered that such a clinker is an exceptional one. It can be readily seen, therefore, that in ground clinker the grains will not be separate grains of any one constituent, as they would be in a mechanical mixture, but that even the finest grains possibly contain some of all of the constituents. Consequently, the activity of the tricalcium aluminate will be retarded to a degree by the inability of the water to reach all of its surfaces. Although what would be its normal activity in the pure condition is thus reduced to certain degree, the other active constituent of the cement—the tricalcium silicate—is being acted upon by the water and the lime is going into solution. This latter very materially modifies the activity of the tricalcium aluminate. If this aluminate in the pure condition is mixed with hydrated lime, in amounts not exceeding 10 per cent, and be then gaged with water, a very smooth, plastic paste, which hardens in air quite similarly to portland cement, is obtained. This action is strikingly different from that of water on the tricalcium aluminate when hydrated lime is not present. It will be recalled that in the latter case a smooth paste was not obtainable, nor one which would harden—on account of the almost instantaneous action of the water and the production of a granular paste composed of grains of unhydrated material protected on their exteriors by a film of hydrated material.

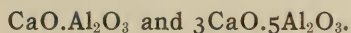
It appears, therefore, that in portland cement the tricalcium aluminate does react to a degree in a manner similar to its action in the pure condition, but that this activity is reduced to a limited degree by the inability of the water to reach all of its surfaces and is masked by the presence of a preponderance of the more slowly acting silicates. The action is also very materially modified by the presence of lime. The latter may have been either

originally present in the cement in the uncombined condition or freed by the water from the tricalcium silicate.

In view of the fact that the tricalcium aluminate, in the pure condition, does not have any hydraulic properties and cannot be readily gaged with water, no test specimens were made for determining its tensile or compressive strength.



There is no great difficulty in preparing $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$. This aluminate when ground reacts so energetically with water that it cannot be readily handled. Some heat is also evolved, but not in the amounts evolved by the tricalcium aluminate. In order to retard somewhat the rapidity of the hydration and thus to permit the molding of the gaged material, it is necessary to use an excess of water. This results in low strengths. If about 3 per cent of ground gypsum is mixed with it, a smaller amount of water is required. The strength in this latter case compares very favorably with that developed by portland cement after the same period of ageing. The products of the hydration of this aluminate are hydrated tricalcium aluminate and hydrated alumina, in other words, during the hydration, alumina splits off and separates as gelatinous hydrated alumina. On account of its rapid set, little further work was pursued with it. Several small burns were made of it although there were no attempts to secure a quantity sufficient for the preparation of neat, sand, or concrete test specimens.



Burnings of small quantities of $\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ showed that both of these set slowly and harden rapidly and attain such high strengths that it was deemed advisable to make burns in a rotary kiln and in sufficient amounts to make concrete specimens for long-time tests. It was also thought advisable to determine the effect of such impurities as silica and iron oxide on the mineralogical composition and on the physical and chemical properties. Eight burns were made, the analyses of the products of which were as follows:

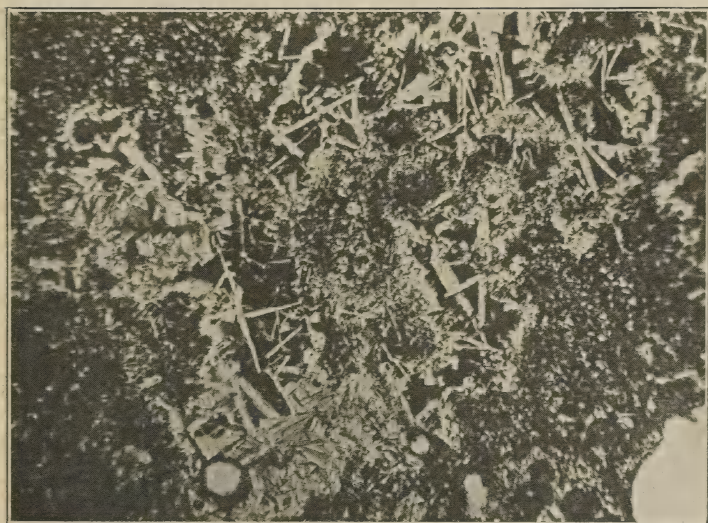


FIG. 2.—Some of the burns produced clinker rich in crystals of $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ and $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$. These cannot be distinguished in thin sections; usually the binary compound predominated.

This figure is a photomicrograph of a thin section of clinker from Burn No. 5. Mag. 90x.

It is of more than passing interest to note that this work was started and the petrographic examination of the clinker was made by Mr. A. A. Klein, former petrographer of the Bureau of Standards, before the paper by Rankin² of the Geophysical Laboratory, giving the fields of stability of all of the compounds of this system, appeared. We were very gratified upon noting in this report that the compounds found in these clinkers by Klein were those that should occur from their composition—according to the results of Rankin (see Fig. 1).

There was no particular difficulty in making any of these burns with the exception of Nos. 4 and 6. Both of these batches had low melting points and consequently had a marked tendency to form "logs" or "balls" in the kiln. In the case of No. 6, a very slight increase in the temperature produced a slag. On

² *Loc. cit.*

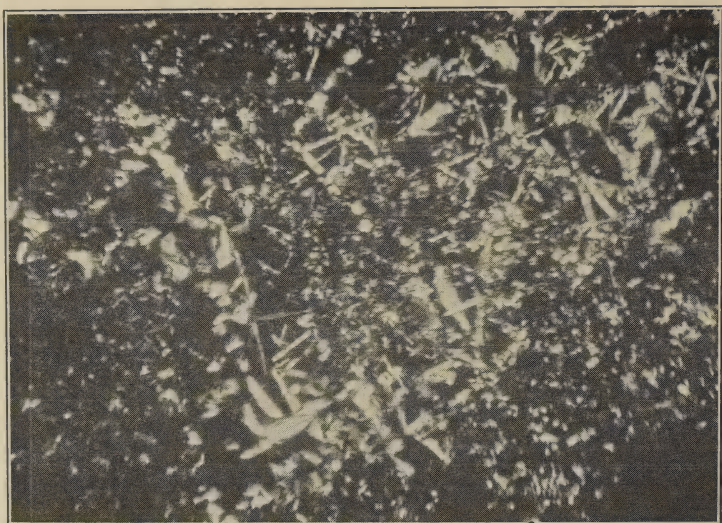


FIG. 3.—The same as Fig. 2, but the Nicol prisms of the polarizing system were crossed.

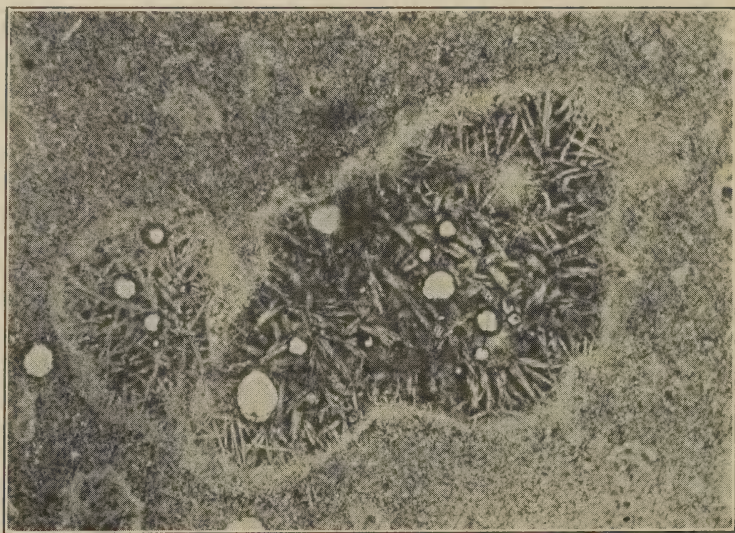


FIG. 4.—Photomicrograph of a thin section of the clinker from Burn No. 3. Mag. 50x.

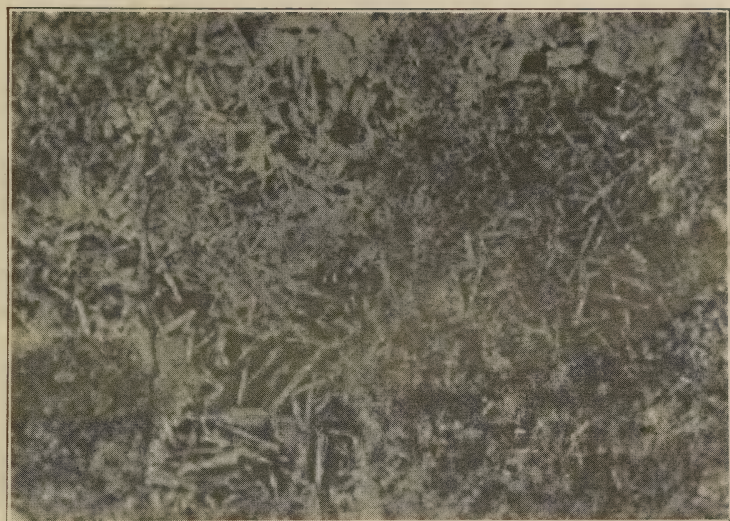


FIG. 5.—Photomicrograph of a thin section of the clinker from
Burn No. 7. Mag. 140x.

account of this low fusion temperature, the β -form of the orthosilicate was not stable and the clinker had a tendency to crumble or dust. This is caused by the inversion of the β -form of the silicate to the γ -form—which is accompanied by an increase in volume of about ten per cent. The material from burn No. 4 crumbled into pieces which were about a quarter of an inch in diameter, while the material from No. 6 was reduced almost completely to a very fine powder. If pieces of the clinker of the latter burn were removed from the hotter parts of the kiln and cooled quickly, the dusting was entirely prevented. The other mixes formed at the temperatures show very satisfactory clinker, the first two (Nos. 1 and 2) and the last ones (Nos. 7 and 8) producing white clinker similar in appearance to that produced in the burning of white portland cement. The structure of some of the clinkers is shown in Figs. 2, 3, 4 and 5.

The times of set of the cements from the above burns as determined by the use of the Gilmore and Vicat needles were as follows:

TABLE 2.

Burn No.	Initial set.				Final set.			
	Giltmore.		Vicat.		Giltmore.		Vicat.	
	Hours.	Minutes.	Hours.	Minutes.	Hours.	Minutes.	Hours.	Minutes.
1.....	0	55	0	25	4	45	2	10
2.....	0	40	0	5	3	50	0	50
3.....	0	25	5	15	*	*	7	5
4.....	0	35	0	10	3	30	1	15
5.....	0	40	0	15	4	45	3	15
6.....	0	7	0	2	0	45	0	12
7.....	6	0	3	45	*	*	*	*
8.....	7	0	*	*	*	*	*	*

* = set between 8 and 24 hours.

The time of set, when studied in connection with composition and constitution, reveals the fact that the mixes low in lime and high in alumina are those which set more slowly. The cement from burn No. 8, which approaches the nearest in composition to $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$, required the longest time for setting, while, as previously noted, $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ sets so rapidly that it cannot be easily handled. The cements from burns Nos. 1 and 2, approaching closely the composition $\text{CaO} \cdot \text{Al}_2\text{O}_3$, have what would be considered a quick initial set but a normal final set. They lie between the $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and the $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ in their setting properties. A comparison of the cements from burns Nos. 5 and 6 or from Nos. 4 and 7, which have closely the same silica content, shows that the time of set is dependent upon the lime—alumina content, the cement with the higher alumina content having the slower set.

In these cements the constituents other than the aluminates do not appear to materially affect any of the properties. The ortho-silicate, when present in any quantities, was in the γ -form which does not hydrate and consequently does not set or acquire strength. The same is also true of the ternary compound $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$. Consequently, these must be considered as non-hydraulic diluents.

Effect of the Addition of Plaster of Paris.—When the investigation was first started it was decided to add 3 per cent of plaster of paris to half of the material from each burn in order to regulate the time of set. Such additions to portland cement usually retard the set but when added to the cements in this

investigation it invariably accelerated the set to a marked degree. This is evident by a comparison of the following times of set (Table 3) of the plastered materials with the times of set previously shown (Table 2):

TABLE 3.
Effect of the Addition of Plaster of Paris on the Time of Set.

Burn No.	Initial set.				Final set.			
	Gilmore.		Vicat.		Gilmore.		Vicat.	
	Hours.	Minutes.	Hours.	Minutes.	Hours.	Minutes.	Hours.	Minutes.
1.....	0	55	0	15	4	55	2	35
2.....	0	30	0	10	2	0	0	50
3.....	0	25	0	20	6	20	3	25
4.....	0	10	0	3	1	40	0	25
5.....	0	15	0	5	3	0	0	30
6.....		flash		flash				
7.....	0	35	0	20	4	30	2	30
8.....	1	5	0	20	4	0	2	45

While the acceleration is more pronounced in the case of the cements high in alumina, all of the work of the Bureau of Standards seems to show that, unless used in excessive amounts, plaster of paris when used alone accelerates the time of set. It would appear necessary that either lime, or a compound that can set lime free in the presence of water, must be present in a cement in order that plaster of paris may act as a retarder. This applies to portland cement as well as to the ones under discussion.

Strength Tests.—For determining the cementing value of these aluminates the following test pieces were prepared:

1. Neat tensile test pieces.
2. 1:3 standard sand mortar tensile test pieces.
3. 1:3 standard sand mortar 2-inch cube compression test pieces.
4. 6" × 12" cylindrical compression test pieces prepared from 1:1.5:4.5 and 1:3:9 gravel concretes.

These were broken at periods as shown in Tables 4, 5 and 6, the results given being the averages of determinations on 3 test pieces. All of the tension and the 2-inch compression specimens, with the exception of half of those broken at 28-day and 26-week periods, were stored under water. These were stored for one-quarter of the period in water and in air for the remainder of

TABLE 4.—TENSILE STRENGTHS OF 1 : 3 STANDARD MORTARS.
Pounds per square inch.

Tested at	24 Hours			7 Days			28 Days			90 Days			26 Weeks			1 Year		
	Water			Water			C. S. ¹ Water C. S.			Water			Water C. S. Water			Water		
Stored in	W. P. ³	P. ²	W. P.	P.	W. P.	P.	W. P.	P.	W. P.	W. P.	P.	W. P.	W. P.	P.	W. P.	W. P.	P.	W. P.
Burn No. 1.....	378	380	403	360	435	730	310	720	440	465	525	595	530	525	525	550	550	550
Burn No. 2.....	275	295	385	305	320	305	595	570	395	480	390	500	375	445	425	470	470	470
Burn No. 3.....	270	195	385	360	525	615	345	585	560	390	575	900	480	665	612	488	488	488
Burn No. 4.....	415	355	280	335	335	345	310	415	375	355	500	400	427	555	435	440	440	440
Burn No. 5.....	155	155	170	155	170	365	175	370	225	172	300	535	163	540	320	185	185	185
Burn No. 6.....	220	175	175	115	280	405	100	285	285	135	245	605	170	315	295	140	140	140
Burn No. 7.....	345	250	295	225	290	560	295	515	350	370	385	575	360	595	390	330	330	330
Burn No. 8.....	330	370	690	390	540	830	280	530	770	195	590	960	380	425	700	460	460	460

¹ C. S. = Stored for $\frac{1}{4}$ of period in water and remainder of period in air.

² P. = Plaster added to the cement.

³ W. P. = No plaster added to the cement.

TABLE 5.—COMPRESSIVE STRENGTHS OF 1 : 3 STANDARD MORTARS.
Pounds per square inch.

Tested at	24 Hours		7 Days		28 Days				90 Days		26 Weeks				1 Year	
	Water		Water		Water	C. S.	Water	C. S.	Water		Water	C. S.	Water	C. S.	Water	
	W.	P. ¹	W.	P.	W.	P.	W.	P.	W.	P.	W.	P.	W.	P.	W.	P.
Burn No. 1.....	3570	2860	5945	2955	3765	6815	2790	4005	3945	3015	5330	6015	3860	4945	3045	2850
Burn No. 2.....	4260	3050	4760	4090	3945	7625	3535	5515	4735	4630	4570	5290	4850	5470	4430	3580
Burn No. 3.....	2240	1630	4940	2450	6475	8000	4655	2540	7180	3210	7760	11050	4630	7100	5315	3015
Burn No. 4.....	4410	3380	4880	2200	5285	6400	2965	5140	4565	2495	3470	3480	2270	4920	3200	2355
Burn No. 5.....	1035	1060	1400	1180	1820	2875	1160	2665	2070	1465	2900	3845	2200	3540	2410	1720
Burn No. 6.....	1340	1060	1260	940	1425	3130	2315	790	1680	925	1895	4345	1475	3055	2310	685
Burn No. 7.....	2165	1870	5140	1720	3930	7085	1415	3610	5205	2630	3605	6090	3080	5430	5225	2010
Burn No. 8.....	2860	2710	8610	4290	7845	10690	3680	7415	8260	4745	6380	8045	4605	7475	8945	4260

¹ See footnote Table 4.

TABLE 6.—COMPRESSIVE STRENGTHS OF 1:6 AND 1:21 GRAVEL CONCRETES.
Pounds per square inch.

Tested at	24 Hours		7 Days		28 Days		90 Days		26 Weeks		1 Year					
	1:6	1:12	1:12 P. ¹	1:6	1:12	1:12 P.	1:6	1:12	1:12 P.	1:6	1:6*	1:12	1:12*	1:12 P.	1:12 P.*	
Burn No. 1**.	2825	3270	4150	4180	3310	
Burn No. 2...	3000	..	1500	4150	..	1890	2480	..	1580	1760	1760	1530	2250	
Burn No. 3...	Soft	2175	3900	4525	4135	
Burn No. 4...	3145	880	1630	3570	1005	1435	2930	875	1280	2565	2965	800	1275	1525	2480	
Burn No. 5...	310	Soft	..	885	225	..	1050	390	..	1270	1460	550	870	
Burn No. 6...	840	275	315	765	275	410	1260	400	700	1515	2110	570	810	600	1055	
Burn No. 7...	1475	455	375	4135	1405	645	4640	1600	800	4450	2035	470	1815	655	1080	
Burn No. 8...	2930	890	470	6010	2270	1740	7050	3980	1760	7610	8220	3930	4445	1470	2450	

* All specimens in these columns were stored for the first 4 months in the damp closet and for the remainder of the period in the air of the laboratory.
All other specimens were stored in the damp closet for the entire period of ageing.

** Cement used in making specimens from Burn No. 1, contained 3 per cent plaster.

¹ Footnote Table 4.

the period. The concrete specimens, with the exception of some of those tested at the end of a year, were stored in a damp closet. When it was noticed that some of the concrete specimens were showing a retrogression in strength after ninety days' storage in the damp closet, it was thought advisable to determine the effect of drying out on the strength of the specimens. A set of test pieces was therefore removed from the damp closet and stored in the air of the laboratory until the end of a year when they were broken. In practically all cases, similar test specimens were made of both the plastered and unplastered cements. Where this was not the case, it is shown in the tables.

Neat Cements.—The results of the tests of the neat specimens are not given. These were eliminated on account of the fact that at no period does there seem to be any relation between the strength developed by a cement as shown by a neat tension test piece and the strength which it may develop in a mortar or concrete. Such has also been found to be the case with portland cement and consequently the present revised specifications of both the Government and the American Society for Testing Materials for the latter no longer recognize or require a neat test piece. The following examples (Table 7) showing the strength of certain test pieces made from the cements containing no plaster, indicated in pounds per square inch at the end of one year, will illustrate this:

TABLE 7.

Burn No.	2	4	6	7	8
Neat tension.....	145	960	445	700	130
1:3 Mortar tension.....	425	435	295	390	700
1:3 Mortar compression.....	4430	3200	2310	5225	8945
1:6 Concrete compression.....	3220	2965	1440	4650	6720

A satisfactory explanation of this behavior is not at hand. Some have attempted to explain it by a nice distinction (?) between the "adhesive" and the "cohesive" strength developed by a cement, assuming that one with high "adhesive" strength gives a high testing mortar or concrete whereas one with a high "cohesive" strength gives a high testing neat specimen. However, it is rather difficult to appreciate such a distinction.

The examination of the data of these tables shows as the

most striking feature the high strength at early periods of all of the mortars and concretes with the exception of those made from cements Nos. 3 and 5. At the present time, Standard Specifications for portland cement have no requirements for strength specimens other than the tensile mortar briquettes. These require that the 1:3 Standard Ottawa sand briquette should have a strength of at least 200 pounds per square inch at the end of 7 days and at least 300 pounds per square inch at the end of 28 days. In Table 4 it is shown that the materials from 4 of the 8 burns develop a greater strength in 24 hours than is required of portland cement in 28 days. The strengths developed by the other kinds of test pieces used are relatively high when compared with the same kind of specimens made from portland cement. Generally, cements Nos. 1, 2, 4, 7 and 8 develop as great a strength in any form of test piece in 24 hours as portland cement will develop in 28 days.

Effect of Plaster.—Those specimens made from the cements to which plaster had been added and which had been stored in water continuously did not usually develop as high strength as the specimens made from the cements from which the plaster had been omitted. This is more pronounced in the case of the compressive than in the tensile specimens.

Effect of Storage.—The storing of the specimens in the air of the laboratory—after storage in water for about one-quarter of the entire period—produced very marked increases in strength over that developed by the specimens stored in water for the entire period. A 50 per cent increase was common and in some cases it exceeded 100 per cent. In passing, it might be mentioned that German specifications for portland cement require that the 28-day test pieces be stored for the first day in the damp closet, then for 6 days under water and the remainder of the time in the air of the laboratory. It is claimed that such storage follows more closely the manner in which mortar or concrete would be handled in practice. However, seasonal or even daily changes in the atmospheric humidity render such storage in the air open to serious criticism. These changes materially reduce the possibility of reproducing results at different times or places from the same cement.

Generally, the concrete specimens showed a decrease in strength with age when stored in the damp closet. This is not surprising when the nature of the hydration of these cements is remembered. This consists in the splitting off of the alumina from the aluminates and its separation as gelatinous hydrated alumina and the formation of hydrated tricalcium aluminate. The latter, until late periods when it tends to change to a crystalline form, is also gelatinous. All of these gelatinous or colloidal products of hydration which form the cementing materials act as any other glue. In the presence of too great amounts of moisture the latter is absorbed and in the presence of small amounts it is given up. Whether water is absorbed or given up by the colloid depends upon the amounts in the colloid and in the gaseous phase. When cements, such as those under consideration, form large amounts of colloid, it follows that the changes caused by moisture will be very pronounced. With the taking up of large amounts of moisture the strength of the specimens will be materially reduced. When the colloid dries out—provided the drying is not carried too far—there is an increase in strength. Just as the moisture content of the atmosphere does not materially affect the strength of an organic glue (such as fish or bone glue) so also it does not decidedly change the strength of mineral glue unless it contains too great amounts of water.

There was not a sufficiently large number of burns in the series to permit of much generalization in regard to the relations between mineral composition or constitution and strength. It is quite evident, however, that the cements with the higher alumina contents develop the higher strengths. The strength is decreased by increasing the silica content—especially if the silica replaces the alumina. However, when silica must be introduced, much better results are obtained by keeping the alumina content constant and replacing lime. The one essential in the composition is to keep the content of alumina such that the composition will approach that of $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$.

High Strength Cements.—Some of the strengths developed by the cements were so high that they are worthy of special citation. Cement No. 8 gave a 1:3 mortar which developed a tensile strength of 770 pounds per square inch at ninety days and 960

pounds per square inch at twenty-six weeks (by the combined storage), and a compressive strength of 8,610 pounds at 7 days and 10,690 pounds at twenty-eight days (by the combined storage) and a 1:6 concrete with a strength of 6,010 pounds at 7 days and 8,220 pounds at one year (by the combined storage). Cement from burn No. 4 gave a 1:6 concrete having a strength of 3,145 pounds in twenty-four hours. The average twenty-four-hour strengths of the 1:6 concretes of cements from burns Nos. 1, 2, 4 and 8 was 3,000 pounds. It should be borne in mind that the above figures are the averages of determinations on 3 test pieces and consequently some individual test pieces gave higher strengths.

CONCLUSION.

It appears from this investigation that it is possible to make, by a method and equipment differing in no manner from that used in making portland cement, cements giving in twenty-four hours strengths as high as those usually developed by portland cements in twenty-eight days—either as a mortar or concrete. This quick-hardening cement is not quick-setting. It differs from portland cement in being a calcium aluminate high in alumina (preferably 55 to 75 per cent). The presence of silica or iron oxide is not desirable but they may be present in amounts up to 15 per cent—provided they replace the lime and not the alumina.

The commercial possibilities of such a cement are not very promising on account of the lack of a widely distributed supply of alumina. While the actual cost of manufacture would not exceed that of portland cement, the cost of the alumina alone would so raise the ultimate cost of the cement that the use of the finished product for any except very special purposes would be precluded.

This opportunity is taken to acknowledge the valuable assistance rendered by Messrs. Klein, Peck and Tucker at various times while the investigation was under way.

NOTE ON CERTAIN CHARACTERISTICS OF PORCELAIN.¹

By A. V. BLEININGER, Pittsburgh, Pa.

Porcelains vary widely in their physical properties such as modulus of elasticity, coefficient of thermal expansion, heat conductivity and electrical resistance at different temperatures. It is not uncommon for instance, to find differences in the modulus of elasticity as far apart as 6,600,000 and 1,200,000. Again, the coefficient of thermal expansion is subject to decided variations for different porcelains as well as for the same material at different temperatures. With reference to the electrical conductivity, the values observed for different temperatures are subject to equally wide variations.

These facts are not at all surprising and are explained by the various stages of development represented by different porcelains. In practically all of them we have conditions far removed from such equilibria as we find in glasses depending upon the composition, the fineness of grinding and intimacy of blending, the rate and the ultimate temperature of firing, and finally the rate of cooling. As a result, the amounts of undissolved quartz or cristobalite, of glassy matrix, of undecomposed clay and of sillimanite fluctuate within wide variations. It is obviously of great importance whether the quartz content is high or low, whether it is comparatively coarse or fine, whether the percentage of feldspar is small or large or whether additional or different fluxes are introduced, and last but not least, what the temperature treatment has been. It is only through more refined and exact measurements that we may obtain a clear notion of the relation between the physical properties of porcelain and the several factors governing them.

In the low-fired porcelains—those fired to about cone 10—it is evident that the amount of undissolved quartz is comparatively large and that of sillimanite small. It is to be expected, therefore,

¹ By permission of the Director, Bureau of Standards.

that this product is subject, upon heating, to the changes in specific volume coincident with the transformations of quartz and cristobalite. It is not unlikely that some of this type of porcelain, when made into heavy pieces, is in a state of stress—due to its heterogeneous structure which has not been modified by high temperature treatment. It is to be expected, on the other hand, that the structure would gradually approach a more balanced, because more homogeneous, state, as higher firing temperatures, which cause far-reaching solution of the quartz and practically complete dissociation of the clay substance into sillimanite, are employed. The development of the latter mineral is desirable owing to its stability, being subject to no transformation changes, its density, 3.031, and its low coefficient of thermal expansion.

The undesirable characteristics of quartz in heavy porcelains are well understood by the manufacturers of sanitary ware who avoid its introduction as much as possible and insist upon the use of French flint—a partially amorphous modification of silica which inverts into cristobalite much more quickly and probably is also dissolved more readily by the fused feldspar. It is not unlikely that the objectionable property of “dunting” and its minor manifestations do not appear until the amount of quartz exceeds a certain value which has not yet been established. In the case of electrical porcelain subject to high tensions, it is more than likely that the permissible content of free quartz remaining in the porcelain is very much lower if maximum stability is desired. In advocating a high clay content for chemical porcelain subject to severe duty, E. T. Montgomery, therefore,¹ proceeds on sound principles and his conclusions deserve careful attention.

In the Pittsburgh laboratory of the Bureau of Standards a large series of porcelains have been made in which quartz has been replaced both by clay and by synthetic sillimanite. In both cases porcelains of excellent stability have been obtained as shown by the resistance of the bodies to sudden heating and cooling. Particularly was this the case by the use of the sillimanite which was prepared by grinding together 258 parts of kaolin, 102 of anhydrous alumina and 7.2 of boric acid, and heating the mix-

¹ *Trans. Am. Ceram. Soc.*, 18, 88-92 (1916).

ture to the softening temperature of cone 20. The calcined material consisted largely of sillimanite with a small amount of uncombined alumina. It was again ground and introduced in the body, replacing the flint. As a type, these porcelains, especially that in which 40 per cent of sillimanite calcine was used together with 40 per cent of clay and 20 per cent of flux, when fired to cone 16, not only showed excellent resistance to sudden heating and cooling but also high mechanical strength. At the same time the sillimanite increased the firing range of feldspar porcelain decidedly. By raising the amount of sillimanite to even larger proportions, porcelains of still more marked stability could be produced. Similar results were obtained through the introduction of other minerals not subject to molecular transformations, such as fused alumina, zirconium oxide, etc. The thermal expansion is decreased with the replacement of quartz by such constituents. The body obtained with the use of the zirconia seemed to be especially desirable for purposes where high mechanical strength was necessary.

It has been known for some time that the dielectric strength of porcelains is greatly reduced upon heating. Messrs. Henderson and Weimer¹ found that when heated from 24° to 275° C, a body fired to cone 9 showed a reduction in the puncturing voltage down to $\frac{1}{30}$ of the initial value. The same experience holds true also for the electrical resistance of vitrified bodies. In fact, the conductivity of such materials increases very rapidly with temperature—according to the law of compound interest at the rate of about 2 per cent per degree C. That this introduces an important factor in the case of porcelains exposed to higher temperatures, such as spark plugs, high tension insulators used in Cottrell process installations, etc., is obvious.

In order to secure information concerning the effect of composition upon these phenomena, a large number of porcelains were made and tested. The specimen used for this purpose was a cup of 60 mm. outside diameter, 65 mm. height and having a thickness of wall of 2.5 mm. The cup was placed in a suitable electrically heated furnace. Electrical contact was provided by

¹ *Trans. Am. Ceram. Soc.*, **13**, 469-475 (1911); also Weimer and Dunn, *Ibid.*, **14**, 280-292 (1912).

the use of molten solder on the inside of the cup and its immersion in a shallow metal bath on the outside.

Alternating current, 60 cycle, of 500 volts, was employed—since direct current gave rise to disturbing polarizing effects. The current passing through the porcelain was measured by means of a very sensitive milliammeter or a dynamometer wattmeter. The temperature was determined by means of two insulated thermocouples immersed in the molten solder of the inside of the cup.

The results of the resistance measurements were plotted as the $\log_{10} R$ against the temperature, in degrees C. The plots were approximately straight lines expressed by the relations

$$\log_{10} R = a - bt,$$

where R = resistance of the specimen, in ohms,

t = temperature in degrees C, and a and b are constants.

By computing a resistivity factor, based on the dimensions of the cup, it was possible to calculate the resistance per cubic centimeter of the porcelain. The criterion used in comparing the merits of each body was the temperature Te at which the material has the definite resistance of one megohm per centimeter cube.

The electrical measurements and computations were made in the electrical laboratory of the Bureau of Standards at Washington.

A characteristic curve for a feldspar porcelain is shown in the diagram of Fig. 1, for which the value $Te = 335^\circ \text{C}$. Upon studying the resistance curves of a number of porcelains it was soon apparent that the feldspar was the important factor in lowering the electrical resistance at these temperatures. Invariably, the higher the feldspar content the lower was the resistance and the value Te . By eliminating the feldspar and carrying the maturing temperature to a high point, say cones 18–20, bodies of good resistance at the temperatures involved were obtained. The same result was reached when the feldspar was replaced by synthetic silicates containing beryllium oxide, magnesia or other alkaline earths. Through the elimination of the feldspar it was found possible to reach a Te value as high as 800°C , which is quite satisfactory when one considers that fused quartz gave the result of 880°C .

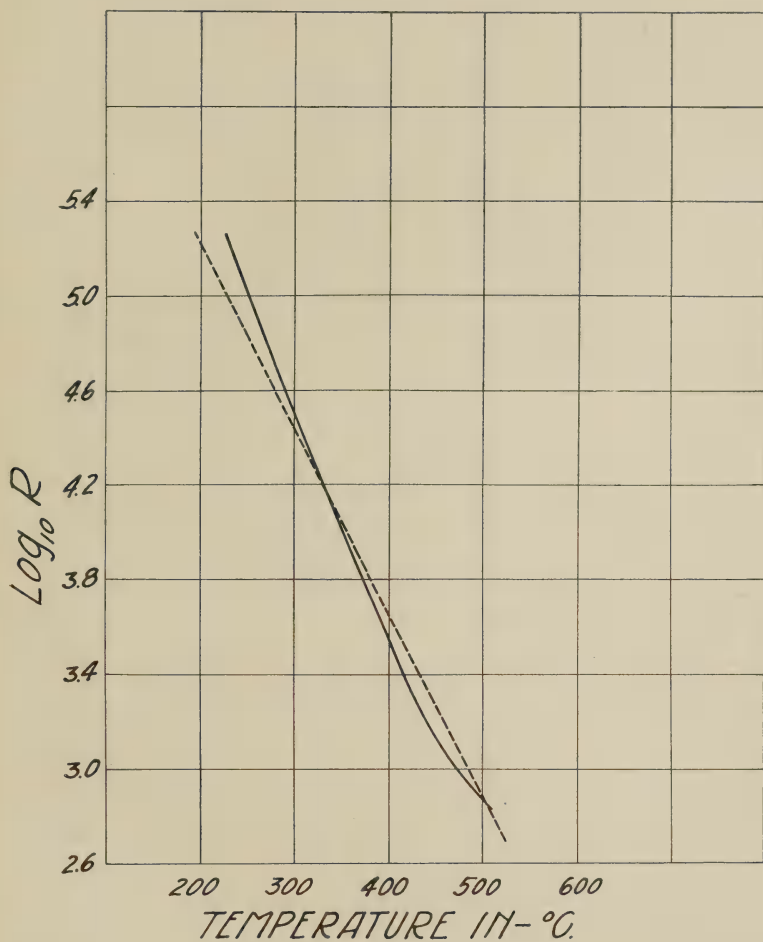


FIG. 1.

It also appeared that with higher feldspar content the polarization phenomena became more prominent, indicating clearly that this constituent of porcelain plays a rôle of an electrolyte. It is evident, therefore, that for conditions where a high tension porcelain insulator is exposed to elevated temperatures it is neces-

sary to reduce the content of the feldspar and to replace it by some other flux.

For porcelains intended to be used under severe electrical and heat conditions, it would appear desirable, therefore, to eliminate both the quartz and the feldspar as constituents of the body in the manner suggested above.

ENAMELS FOR CAST IRON.¹

By HOMER F. STALEY, Washington, D. C.

I. TIN ENAMEL COMPOSITIONS.

Basis of Classification.

The tin enamel compositions for cast iron in common use have, for the most part, been developed in factory practice through long years of patient cut-and-try experiments by men who had little knowledge of chemistry and less of physics to guide them. In recent years a few ceramic engineers have entered this field and have materially reduced the cost of the enamels in use. This reduction in cost, however, has consisted mainly in substituting cheap forms of chemicals for more expensive forms and the elimination of a few expensive ingredients of little value. The general types of enamels had been too thoroughly worked out in practice to permit any radical innovations. The fact that these types have stood the test of time and are really a "survival of the fittest" is in itself proof that they must conform, at least roughly, to the laws of physics and chemistry applicable to enamel compositions.

Many factors determine the availability of an enamel, such as fusibility, luster, coefficient of expansion, strength, elasticity, color, and hardness and resistance to chemical agents. Enamel compositions might be classified according to the relation of compositions to any one of these factors, but the most obvious relation is that of composition to luster, as dependent on the ability of the enamel to remain glassy and not devitrify during working and cooling. Of course, all of the other factors have a modifying effect in determining the actual compositions used. In fact, any enamel composition is a compromise.

As stated under the discussion of luster,² boric oxide and lead oxide are the only fluxing oxides that can be present in enamels

¹ By permission of the Director, Bureau of Standards.

² THIS JOURNAL, I, Sept. (1918).

in large amounts without causing devitrification. The amount of the other fluxing oxides that may be added without causing devitrification is so small that it is practically impossible to make a satisfactory enamel for cast iron unless the sum of these two oxides is above a certain minimum. Boric oxide is always used, and tin-bearing enamel compositions fall into three general types: (1) Leadless enamels, (2) low lead enamels, (3) high lead enamels (Table 1). Of course it is understood that the following compositions (Table 1) are for powdered enamels to be applied to cast iron:

The Leadless Type.—The leadless type of enamel has been developed in Germany. It is characterized by a very high boric oxide content. Since the enamel is so high in boric oxide, it would have a very low coefficient of expansion and would therefore tend to chip, other factors, such as strength and elasticity, being equal, if this were not corrected in the rest of the composition. Therefore, the German enamels high in boric oxide are high in sodium oxide and cryolite, both of which have a very decided tendency to raise the coefficient of expansion of enamels. Since boric oxide has a favorable effect on the strength and elasticity of enamels, the unfavorable effect of a large amount of sodium oxide on these properties is counter-balanced. On account of the solvent action of glasses high in sodium oxide on tin oxide, the amount of the latter substance is high, compared to American practice.

Enamel 1 (Table 1) published by Dr. Julius Grünwald¹ who has written extensively on German enameling practice, is a formula of this type. Clay is seldom used in making enamel melts in America, and the amount of tin oxide in Grünwald's formula would be considered excessive. A formula such as Enamel 2 conforms more nearly to American ideas of what a leadless enamel high in boric oxide should be.²

The Low Lead Type.—Since lead oxide is present in considerable amounts in the low lead type of composition, the boric oxide can be lower than in the previous type without danger of

¹ *Stahl u. Eisen*, 30, 1204.

² H. F. Staley and G. P. Fisher, *Trans. Am. Ceram. Soc.*, 15, 626 (1913).

devitrification taking place. The lead oxide generally runs under 10 per cent and the boric oxide over 8 per cent. In American practice, considerable zinc oxide is generally used in this type of enamel. Enamel 3 is an old formula for this type of enamel and Enamel 4 is a modern derivative of the same formula.

The High Lead Type.—In the high lead type of enamel the lead oxide runs from 16 to 25 per cent of the melted weight of the enamel. Since the lead oxide is so high the boric oxide can be low (around 6 per cent of the melted weight), as in Enamel 5, without danger of devitrification. However, on account of considerations of strength and elasticity, the boric oxide is often kept as high as 8 per cent in high lead enamels as in Enamels 6 and 7. The amounts of the other fluxing oxides vary widely, but any one seldom exceeds 10 per cent. This is the type of powdered enamel for cast iron most commonly used in this country and many formulas might be given, but Enamels 5, 6 and 7 (Table 1) are typical.

TABLE 1.—TIN ENAMEL FORMULAS.

Raw batch for 1000 pounds melted.

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	No. 7.
Potash feldspar.....	340	410	380	400	380	380	380
Clay.....	55
Sodium nitrate.....	5.5	30	..	30	25	30	30
Soda ash.....	21	..	30	90	50	30	30
Borax.....	555	240	225	225	165	215	215
Cryolite.....	110	120	10	40	..	30	..
Fluorspar.....	5.5	..	85	85	120	50	50
Ammonium carbonate...	8	..	1
Magnesium carbonate...	5.5
Tin oxide.....	188.6	83	92	94	85	90	90
Boric acid.....	..	220
Zinc oxide.....	..	125	108	108	60	105	50
Quartz.....	15
Potassium nitrate.....	60
Potassium carbonate...	30
Red lead.....	82	94	175	168	255
Sodium silico fluoride...	40
Manganese dioxide.....	1
Arsenic oxide.....	6
Barium carbonate.....	75	50	50
	1294.1	1228	1165	1166	1135	1148	1150

TIN ENAMELS.

Percentage Composition.

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	No. 7.
Silica.....	24.46	26.5	26.08	25.88	24.58	24.58	24.58
Alumina.....	8.44	7.5	7.00	7.36	7.00	7.00	7.00
Potassium oxide.....	5.66	7.0	11.22	6.76	6.42	6.42	6.42
Sodium oxide.....	10.41	5.0	5.38	9.95	6.50	6.31	6.31
Boric oxide.....	20.33	21.2	8.23	8.23	6.04	7.87	7.87
Aluminium fluoride.....	4.40	4.8	0.40	1.60	...	1.20	..
Sodium fluoride.....	6.60	7.2	2.36	2.40	...	1.80	..
Magnesium oxide.....	0.26
Tin oxide.....	18.86	8.3	9.20	9.40	8.50	9.00	9.00
Zinc oxide.....	...	12.5	10.80	10.80	6.00	10.50	5.00
Lead oxide.....	8.00	9.20	17.10	16.50	25.00
Silicon fluoride.....	2.24
Calcium fluoride.....	0.55	...	8.50	8.50	12.00	5.00	5.00
Manganese oxide.....	0.10
Arsenic oxide.....	0.60
Barium oxide.....	5.83	3.88	3.88
	99.97	100.0	100.00	100.08	99.97	100.06	100.06

TIN ENAMELS.

Empirical Chemical Formulas.

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	No. 7.
K ₂ O.....	0.188	0.187	0.230	0.130	0.130	0.140	0.153
Na ₂ O.....	0.773	0.423	0.222	0.345	0.201	0.294	0.230
CaO.....	0.021	...	0.212	0.200	0.295	0.132	0.145
MgO.....	0.018
BaO.....	0.073	0.052	0.059
ZnO.....	...	0.390	0.258	0.244	0.142	0.269	0.140
PbO.....	0.076	0.081	0.159	0.153	0.273
MnO.....	0.002
Al ₂ O ₃	0.332	0.260	0.138	0.150	0.132	0.157	0.156
SiO ₂	1.255	1.118	0.882	0.790	0.785	0.847	0.920
B ₂ O ₃	0.890	0.766	0.229	0.216	0.155	0.231	0.253
SnO ₂	0.383	0.140	0.118	0.114	0.107	0.124	0.135
F ₂	0.519	0.436	0.356	0.266	0.295	0.218	0.144

II ANTIMONY ENAMEL COMPOSITIONS.¹

Sodium Metantimonate Enamel Compositions.

Sodium metantimonate has been employed extensively in this country during late years as an opacifying agent for enamels

¹ For detailed treatment of color phenomena, etc., see Staley, *Trans. Am. Ceram. Soc.*, 17, 173-189 (1915).

for cast iron. The compositions used may be divided into three types: the leadless, the low lead, and the medium lead (Table 2).

The Leadless Type.—In Germany leadless enamels in which sodium metantimonate is the opacifier have been derived from the leadless tin enamels, similar to Enamel 1 (Table 1), very high in boric oxide and containing only one or two other fluxes. In this country, however, leadless enamels containing sodium metantimonate have been derived from the complicated formulas in use for tin enamels, by the substitution of other fluxes for lead oxide. This has resulted in complicated formulas, rather high in boric oxide and generally high in zinc oxide. Boric oxide is increased as lead oxide is decreased because, when used in large amounts, it not only does not itself crystallize but it makes the enamel more viscous and thus prevents the crystallization of other compounds that may have been used to partially replace lead oxide.

The zinc oxide is increased as the lead oxide is decreased in order to maintain the strength and elasticity of the enamel. By using a complicated formula the amount of each of the other fluxing oxides is kept low, so that tendency for their compounds to crystallize and cause dull luster is lessened. Enamel 8 (Table 2) is a typical composition.

The Low Lead Type.—The low lead type of composition contains 3 to 5 per cent of lead oxide; the boric oxide and zinc oxides are usually a little lower than in the leadless type. The amount of each of the other fluxing oxides is kept low. Enamel 9 is a typical example. In this the percentage of sodium oxide is approaching the danger limit as far as luster of the enamel is concerned. Its use would be safer if 50 pounds of borax were substituted for the 45 pounds of soda ash. This would give boric oxide and sodium oxide contents like those in Enamel 8.

The Medium Lead Type.—In the medium lead type of composition, the lead oxide runs between 5 and 12 per cent. The boric oxide is slightly lower than in the previous type, but still higher than in high lead tin enamels, and the percentage of each

of the other fluxing oxides is kept low. Enamels 10 and 11 are typical compositions. It will be noted that in Enamel 11 no calcium carbonate is used, but that a larger amount of fluorspar is used than in the other compositions. Thus the calcium content is maintained at the proper point to give good color and opacity.

Oxide of Antimony Enamel Compositions.

The essential difference between sodium metantimonate enamel compositions and those in which oxide of antimony is used as the chief opacifier is that the latter contain much larger amounts of sodium nitrate. Corresponding reduction is made in other sodium compounds so that the total sodium oxide content remains about the same. This larger nitrate content may mean that the oxide of antimony is converted into sodium metantimonate ($\text{Na}_2\text{O} \cdot \text{Sb}_2\text{O}_5$) or simply into antimony pentoxide (Sb_2O_5). Incidentally the oxide of antimony enamels which the writer has found in actual use in factories contain considerable cryolite, and therefore the percentage amount of oxide of antimony can be lower than in the case of sodium antimonate compositions containing little or no cryolite.

TABLE 2.—ANTIMONY ENAMEL FORMULAS.

Raw batch for 1000 pounds melted.

	No. 8.	No. 9.	No. 10.	No. 11.	No. 12.	No. 13.	No. 14.	No. 15.
Potash feldspar.....	390	390	390	375	410	410	410	400
Sodium nitrate.....	35	35	35	25	70	70	90	75
Borax.....	350	300	250	275	350	300	240	230
Barium carbonate.....	80	80	70	100	80	75	80	80
Zinc oxide.....	140	110	85	70	140	100	100	92
Calcium carbonate.....	30	30	30	..	30	30	30	25
Fluorspar.....	73	73	..	100	60	73	45	55
Sodium antimonate.....	120	120	120	110
Soda ash.....	..	45	55	25	..	25	30	20
Red lead.....	..	31	85	102	..	46	82	117
Calcium fluoride.....	73
Cryolite.....	40	40	45	45
Antimony oxide.....	60	60	64	58

1218 1214 1193 1182 1240 1229 1216 1197

ANTIMONY ENAMELS.

Calculated percentage composition, melted.

	No. 8.	No. 9.	No. 10.	No. 11.	No. 12.	No. 13.	No. 14.	No. 15.
Silica.....	25.23	25.23	25.23	24.26	26.53	26.53	26.53	25.88
Alumina.....	7.18	7.18	7.18	6.90	7.54	7.54	7.54	7.36
Potassium oxide...	6.59	6.59	6.59	6.34	6.93	6.93	6.93	6.76
Sodium oxide.....	8.94	10.75	10.52	8.57	8.22	8.86	8.91	7.62
Boric oxide.....	12.81	11.00	9.15	10.06	12.81	11.00	8.78	8.42
Barium oxide.....	6.21	6.21	5.44	7.77	6.20	5.83	6.21	6.21
Zinc oxide.....	14.00	11.00	8.50	7.00	14.00	10.00	10.00	9.20
Calcium oxide.....	1.68	1.68	1.68	..	1.68	1.68	1.68	1.40
Antimony oxide...	10.00	10.00	10.00	9.24	6.00	6.00	6.40	5.80
Lead oxide.....	...	3.00	8.40	10.00	...	4.50	8.00	11.50
Calcium fluoride...	7.30	7.30	7.30	10.00	6.00	7.30	4.50	5.50
Sodium fluoride....	2.40	2.40	2.70	2.70
Aluminium fluoride	1.60	1.60	1.80	1.80
	99.94	99.94	99.99	100.14	99.91	100.17	99.98	100.15

ANTIMONY ENAMELS.

Empirical chemical formulas.

	No. 8.	No. 9.	No. 10.	No. 11.	No. 12.	No. 13.	No. 14.	No. 15.
K ₂ O.....	0.127	0.125	0.128	0.129	0.132	0.133	0.135	0.133
Na ₂ O.....	0.263	0.311	0.310	0.267	0.288	0.310	0.328	0.293
CaO.....	0.225	0.223	0.228	0.246	0.194	0.227	0.163	0.180
BaO.....	0.072	0.072	0.066	0.100	0.073	0.069	0.074	0.075
ZnO.....	0.313	0.244	0.193	0.166	0.313	0.224	0.228	0.214
PbO.....	...	0.025	0.075	0.092	...	0.037	0.072	0.105
Al ₂ O ₃	0.129	0.127	0.130	0.131	0.150	0.151	0.157	0.158
SiO ₂	0.761	0.754	0.777	0.777	0.801	0.803	0.818	0.808
B ₂ O ₃	0.332	0.282	0.240	0.277	0.332	0.287	0.231	0.225
Sb ₂ O ₅	0.063	0.063	0.064	0.062	0.038	0.038	0.041	0.038
F ₂	0.170	0.169	0.173	0.246	0.238	0.269	0.188	0.216

These compositions can be divided into the same three types as sodium antimonate enamels, the characteristics of each type being practically the same as before. Enamel 12 (Table 2) is typical of the leadless type, Enamel 13 of the low lead type and Enamels 14 and 15 of the medium lead type.²

² Compare R. E. Brown, *Trans. Am. Ceram. Soc.*, **14**, 740-755; H. F. Staley, *Ibid.*, **17**, 173-189.

A METHOD FOR THE DETERMINATION OF AIR IN PLASTIC CLAY.

BY H. SPURRIER.

Although almost universally used in the pottery industry in the preparation of plastic clay bodies, the potters pug-mill is not an efficient piece of apparatus. Though a certain amount of pugging is necessary, an over-liberal treatment may injure an otherwise good body by the introduction of an excessive amount of air. In experimenting with pug-mills it was found desirable to determine the actual air content of various samples of clay. In making this determination it was evident that a method which actually separated and measured the contained air would be the most likely to give satisfaction. With this in view, some experiments were made in order to determine the feasibility of disintegrating samples of pugged clay in boiling water. So encouraging were the results that it was determined to extend the preliminary work so as to include the measurement of the contained air in extruded samples, thrown samples, and also in sections cut from clay filter press leaves. These simple experiments afforded some quite unexpected information in regard to the structure of the blanks examined.

The manner in which a piece of clay slakes down in water indicates at once the method of its formation. In an extruded blank, made on a special machine, we observed that the separation of the clay particles took place along longitudinal lines—indicating that the air cavities lie along parallel planes (Fig. 1, *a*). Thrown blanks exhibited very plainly the spiral striae formed in the process of throwing (Fig. 1, *b*). A section cut from a filter-press leaf did not slake or disintegrate in boiling water but remained indefinitely in the water without slaking down (Fig. 1, *c*). This latter case shows clearly that it is the disruptive effect of the gas vesicles, expanding under increasing temperature, that causes the clay to slake down, thus allowing the gases to escape.

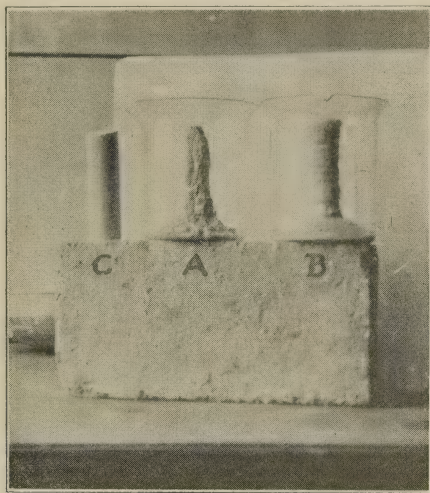


FIG. 1.—Showing the behavior of clay blanks in slaking down in water.

It became evident that if the air separation could be made quantitatively it might be made the basis of a clean-cut determination. Accordingly, an apparatus was assembled to accomplish this end. It was ascertained that kerosene did not have any tendency to slake the clay or in any way disturb it, neither did it dissolve the air.

A heavy 600 cc. flask (Fig. 2, *a*) was fitted with a two-hole rubber stopper. The larger hole, being evenly cupped at the smaller end of the stopper, was fitted with a 7 mm. glass tube just reaching to the bottom of the cup. The smaller hole was fitted with a right-angle bend, one limb extending to the bottom of the flask, the other terminating at a conveniently short distance from the bend; this tube was susceptible of connection with either a kerosene reservoir or a supply of boiling water (Fig. 2, *b*). The larger tube was surmounted by a two-hole rubber stopper entering the enlargement of the measuring tube; the other hole of the stopper was fitted with a glass tube that effected connection with and reached to the bottom of a 2500 cc. bottle (Fig. 2, *c*) containing

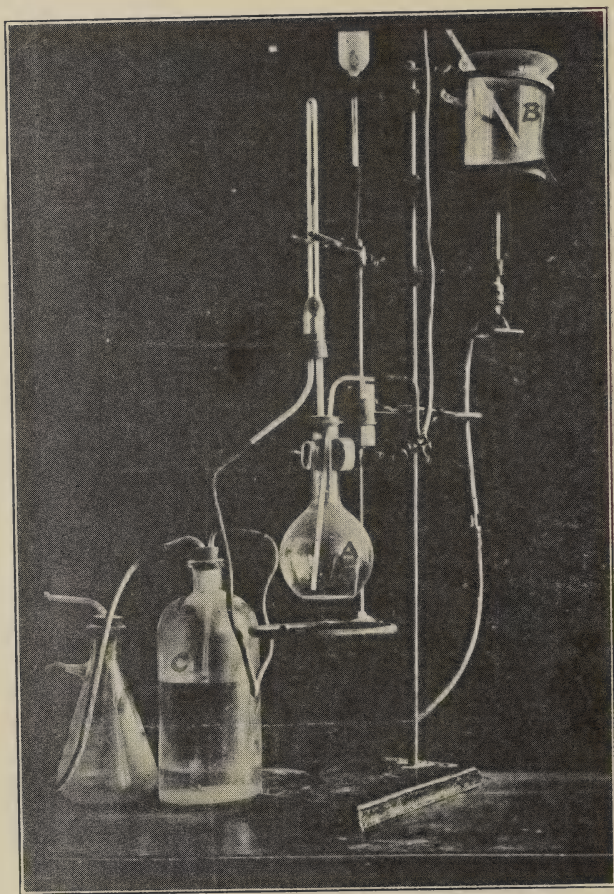


FIG. 2.—Apparatus used in the determination of the air content in clays.

500 cc. of kerosene and connected with a jet-vacuum pump. The whole was mounted on a universal stand as clearly shown. The determination is made as follows:

The duly measured (weighed if desired) blank is placed in the flask filled with kerosene which is then tightly corked. Kerosene is allowed to flow from the elevated reservoir until it overflows

into the 2500 cc. suction bottle. The whole is then turned through an angle of about 100 degrees and more kerosene run in so as to fill the measuring tube and completely expel every bubble of air. The apparatus is then placed in erect position and clamped and the kerosene tube connected with the boiling water in the elevated liter beaker in such a manner that no air enters the tube. This manipulation requires no more dexterity than is called for in an ordinary gas analysis. The boiling water is now run into the flask, completely displacing the kerosene—the excess water running out of the system into the suction bottle—and the screw-cock closed. The disintegration of the clay commences at once with the consequent liberation of the contained gases, which rise to the top of the measuring tube—duly calibrated in 0.1 cc. divisions for a space of 25 cc. and reading from above downward. A water bath is supported around the flask (Fig. 2, *a*) which is occasionally tapped with the finger tips to effect necessary agitation. The vacuum pump is set in operation causing considerable dilatation of the gas bubbles and duly facilitating their collection in the measuring tube. After about fifteen minutes, the vacuum is broken and upon equalizing the pressure by using the vacuum bottle as a leveling bottle, as customarily practiced in gas analysis, the volume of air is read and the temperature taken. The data is now in hand for calculating the volume of gas to normal temperature and pressure or any other basis preferred. The following results illustrate the application of the method:

A sample of air-free filter press clay was passed through a pug-mill and the air content determined to be 9.61 per cent by volume of the clay sample—calculated at room temperature, no correction for the barometer being necessary. On passing this clay through another pug having well-set blades the air content was found to be 9.88 per cent by volume.

Another sample was passed five times through a special pug after which the air content was found to be 13.18 per cent by volume.

The method lends itself admirably to the determination of the proper blade setting of pug-mills and the determination of the soundness of pugged clay insofar as air content is concerned.

JEFFERY DEWITT CO.,
DETROIT, MICH.

DISCUSSION.

PROF. BINNS: I have recently had occasion to take up again the question of using the French rolling table instead of the pug-mill in the preparation of potters clay. There is no question in my mind but that the French rolling table is the ideal machine for preparing clay and its use would overcome a great many of the difficulties arising from the air in the plastic body. It does not, however, prepare the clay as rapidly as the pug-mill and this has been one of the objections to its use.

MR. GORTON: I would like to ask if a determination of the air content was made upon clay which had been wedged by hand?

MR. SPURRIER: No, we do not use the wedging process in our plant at present. At one time we used the wedging process in the preparation of the clay for a special purpose. In this case we noticed that the lamination planes in the blanks were parallel to the axis of throwing and that the distribution of the air was very uneven. It has been our experience that wedging is not a satisfactory process for the preparation of the clay blanks.

MR. BARRINGER: This question of occluded air is, I think, particularly important in Mr. Spurrier's line, which I understand is the manufacture of spark plugs, where the elimination of the air is necessary to the production of the maximum mechanical and dielectric strength. It is not clear to me, however, why it is equally important to eliminate the air from other ceramic wares. I can sympathize with manufacturers of white ware, etc., who claim that the French rolling table process is too slow. Why is not the pug-mill satisfactory for the preparation of the clay for such wares? Would it not be possible to operate a pug-mill under low air pressure and thus gain the desired capacity together with the complete or almost complete elimination of the air?

MR. LOVEJOY: There is one device on the market and a patent pending on another which is designed to do that which Mr. Barringer suggests; that is, to shred the clay to release the air and remove the latter by suction. The inventor who is working on this device claims that laminations and the faulty dry-

ing which results from laminations are largely due to the included air.

MR. SPURRIER: In regard to the removal of the air by the employment of a vacuum, I do not believe it possible to get very good results. When a piece of clay is subjected to a decreased pressure, which we improperly call a vacuum, the air vesicles expand, it is true, but they are not removed. The air vesicle may be dilated but still remains in the clay. It is very interesting to note that if a piece of clay is placed in a bottle in kerosene and subjected to alternating increased and reduced pressure, it will behave like a piece of rubber. The air vesicle is not removed but increases and decreases in size with the variations in pressure.

MR. BROWN: Would it be possible to remove the air from a clay slip in that way?

MR. SPURRIER: Yes, that is being done. If you subject a slip in a bottle to reduced pressure, it will increase in volume, and if you tap the bottle with the knuckles, a leaden sound is given forth, indicating a lack of continuity. If the evacuation has continued long enough and all of the air is removed, the bottle will ring when tapped. The removal of the air from a heavy slip by evacuation is not practicable.

MR. BARRINGER: The statement confirms my opinion that air may be worked from a clay by some such method as kneading but is not readily removed by reducing the outside air pressure. As to pugging under reduced air pressure, I believe that this would involve considerable mechanical difficulty in the operation and maintenance of the apparatus.

NOTES ON SAGGER CLAYS AND MIXTURES.

BY G. H. BROWN, New Brunswick, N. J.

Introduction.

The sagger problem, although an old one, does not appear any nearer its solution than it was several years ago. The sagger losses in our potteries and other ceramic industries is a serious one and the life of the saggars is an important item in the profit and loss columns in most of the plants. It is true that there is considerable variation in the length of life of the saggars used in the different plants, but there appears to be no generally accepted practice particularly as to the kinds of clays used in the sagger mixtures. Frequently, a change in the composition of the sagger mixture is necessitated by inability to secure the clays formerly used and the consequent substitution of new and untried materials in the sagger batches.

In a great many plants, the composition of the sagger mixture is governed for the most part by the cost of the clays—the quality of the clays and their suitability for this purpose being secondary to the price per ton. However, very often, a so-called low-grade or cheap clay will produce a sagger having longer life than some of the so-called high-grade clays sold at fancy prices.

Character of Sagger Failures.

The character of sagger failures may be briefly classified as follows:

1. Breakage due to the rough handling of the unburned saggars in placing in the kiln.
2. Breakage due to the too rapid heating of the saggars during the first burning.
3. Breakage during the cooling in the kilns.
4. Breakage due to rough handling of the saggars in drawing from the kiln and emptying and in again placing in the kiln.

5. Failures due to the deformation of the loaded saggers at the maximum kiln temperatures.

Taking up in order the above types of failures:

1. **Breaking in Handling.**—The breakage in the green state during placing may obviously be reduced by more careful supervision of the placing of the unburned saggers in the kiln. This breakage is, however, governed to a large extent by the strength of the sagger clays in the dried condition and clays having good strength should be used—all other properties being satisfactory. The strength in the dry condition is also governed by the size and proportioning of the grog particles and the percentage of grog used.

2. **Breakage in Heating-up.**—Some of the breakage of saggers may be ascribed to their being too rapidly heated during the first burning. This is especially true if the saggers have not been thoroughly dried before placing in the kiln. It is also governed to a certain extent by the amount of rapid heating which the clays used in the sagger mixture will withstand. The writer has observed instances in which the facilities for drying the saggers were entirely inadequate and, when placed in the kiln, they still contained an appreciable percentage of the water used in tempering the sagger mixture. In starting up the fires in the kiln, this water may be too suddenly converted into steam and cracking of the saggers results.

We must not lose sight of the fact that sagger clays contain chemically combined water, as do all other clays, and that this combined water is only driven off as the kiln reaches a visible red-heat. If the temperature is raised too rapidly during this period the chemically combined water is converted too suddenly into steam, a strain in the sagger is set up, and cracking and breakage result.

3. **Breaking in Cooling.**—From the observations we have made, we are inclined to believe that most of the breakage of saggers takes place during the cooling down of the kilns. Any clay product will crack if cooled rapidly enough. Some, of course, will crack or break more readily than others. Of the many ceramic wares, fused quartz has perhaps the greatest resistance

to temperature changes—this being due to its very low coefficient of expansion and its very regular and uniform expansion and contraction when heated or cooled. A piece of fused silica ware will crack, however, if cooled quickly enough. We find the same to be true of all ceramic wares which must necessarily withstand unusual temperature changes in use. We might mention chemical porcelain, Marquart porcelain, gas mantle rings, spark plugs, etc. Turning to the heavier and cruder clay products, manufactured from fire clays, we find the same to be the case. It is well known that silica brick are very sensitive to temperature changes and crack very readily. It is generally accepted that a fire brick having a high content of quartz or silica will crack and spall more readily than the so-called high-clay fire brick. We also know that some high-clay fire brick are more sensitive to temperature changes than others. Therefore, under the same conditions of cooling, saggars made from one fire clay mixture will crack more readily than saggars made from another mixture. We will discuss the reasons for this later on in the paper.

4. Breakage from Handling.—Some of the sagger breakage is undoubtedly due to the more or less rough handling which the saggars receive in placing in and drawing from the kiln. This breakage may be aggravated by the use of a vitrifying wad-clay and the consequent necessity of pounding the sagger in order to loosen it from the one underneath. It may also take place in setting the sagger on the floor or on the bench. A sagger may not be actually broken by the handling but it may be so weakened that it will crack and break the next time it is fired. Obviously, the reduction of breakage from this source is a question of using the right kind of wad-clay and of supervision of the drawing from and placing in the kiln.

5. Deformation.—Failures through the deformation of saggars—due either to heavy loading or firing to high temperatures—are not so common as those due to cracking or breaking. This type of failure, of course, is more prevalent in those plants firing large and heavy wares and in those plants employing the higher firing temperatures. Our American pottery practice differs markedly from that of Continental Europe in the firing tem-

peratures employed—which are uniformly lower in our ceramic plants. We might say that the average firing temperatures of our kilns is not above cone 10 or 11 and very rarely in this country do we encounter firing temperatures above cone 13 as against cones 16, 17, and 18 reached in Europe. Our sagger problem is, therefore, not analogous to theirs. We must repeat, therefore, that deformation is not the most general type of failure of saggars.

Requisite Properties of Saggars.

Having discussed the character of sagger failures we take up the question of the properties requisite in saggars in order to reduce the failures due to the above. The requisite properties of a sagger may be outlined as follows:

1. Refractoriness.
2. Mechanical strength.
3. Resistance to deformation.
4. Resistance to temperature changes.

1. **Refractoriness.**—The refractoriness of the clays used in a sagger mixture should receive first consideration. Refractoriness has come to mean more than a high melting or softening point.

The investigations on fire clays during the past ten years have led to a very definite classification of our fire clays, not only in accordance with their so-called melting points, but also on the basis of their vitrification or burning behavior at the temperatures at which they are to be used. The fact that one fire clay has a softening point two or three cones higher than that of another fire clay does not necessarily mean that the former will give better service in a sagger mixture. If a kiln of ware is being fired to cone 12, it is immaterial whether the saggars used have a melting or softening point of cone 29 or cone 32. In this case the behavior of the sagger at cone 13 and below is of infinitely more importance than is its behavior at cone 26.

Sagger clays, and all fire clays used as a bond in the manufacture of clay products, may be roughly divided into two classes, insofar as their burning behavior is concerned, *i. e.*, they may be classified as *vitrifying* and *open-burning*. A vitrifying clay is, of course, one which vitrifies at a comparatively low temperature

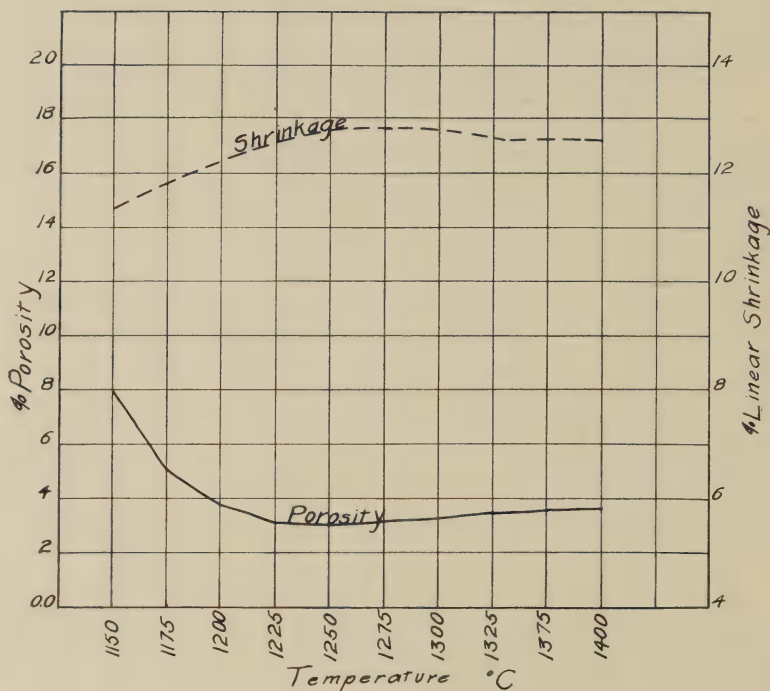


FIG. 1.

and retains its vitrified structure and low porosity over a wide temperature range without swelling or over-burning. In Fig. 1 is shown the burning behavior of a clay of this type. It will be noted that the shrinkage of this clay although high is quite uniform and that the trend of the shrinkage curve conforms quite closely with that of the porosity curve.

In Fig. 2 is shown the burning behavior of an open-burning clay—one which retains a porous structure and high absorption at a comparatively high temperature. The burning shrinkage of this type of clay is usually low and shows little change in firing over a wide temperature range.

In Fig. 3 is shown the burning behavior of a clay which does not fall under the above classification. It will be noted that the porosity of this clay decreases quite regularly with the firing

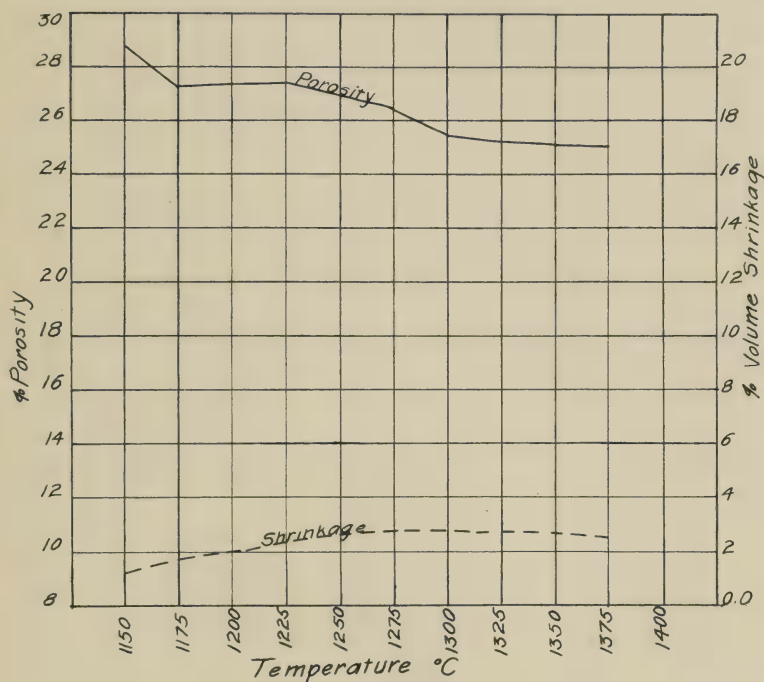


FIG. 2.

temperature until a vitrified structure is attained at a high temperature. The firing shrinkage increases quite regularly with the firing temperature and the shrinkage curve conforms with the porosity curve, *i. e.*, as the porosity decreases, the shrinkage increases. A clay of this type is obviously not well suited to the manufacture of many of our clay products as with each increase in temperature the clay undergoes further shrinkage and consequently does not reach a condition of equilibrium until a high temperature is reached.

In Fig. 4 is illustrated the burning behavior of a clay which is obviously unsuited to the manufacture of saggers or other clay products which are burned to high temperatures. It will be noted that the porosity of this clay decreases somewhat uniformly with the increase in temperature until it reaches the

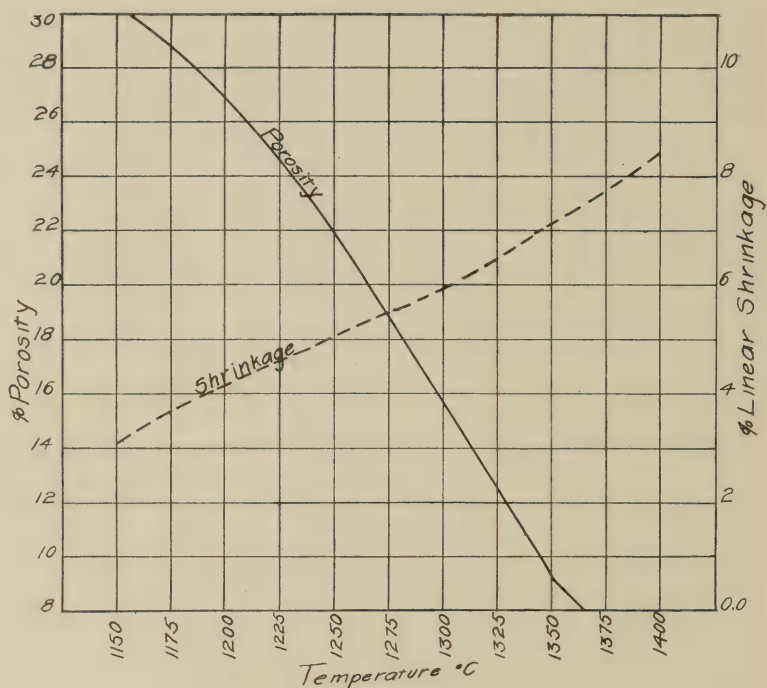


FIG. 3.

minimum porosity, after which the porosity increases rapidly, indicating the development of a vesicular structure.

In view of the wide variations in the burning behavior of the different fire clays, the softening or fusion point is therefore not a safe criterion in the selection of a clay to be used in a sagger mixture.

2. Mechanical Strength.—Under mechanical strength we will consider the resistance of the saggars to breakage during placing and drawing after the first firing. The mechanical strength of a burned sagger in the cold is dependent upon several factors:

1. The extent to which the bond clays vitrify at the finishing temperature of the kiln.

2. The mesh of the sieve through which the grog is sieved and the proportioning of the grog particles.

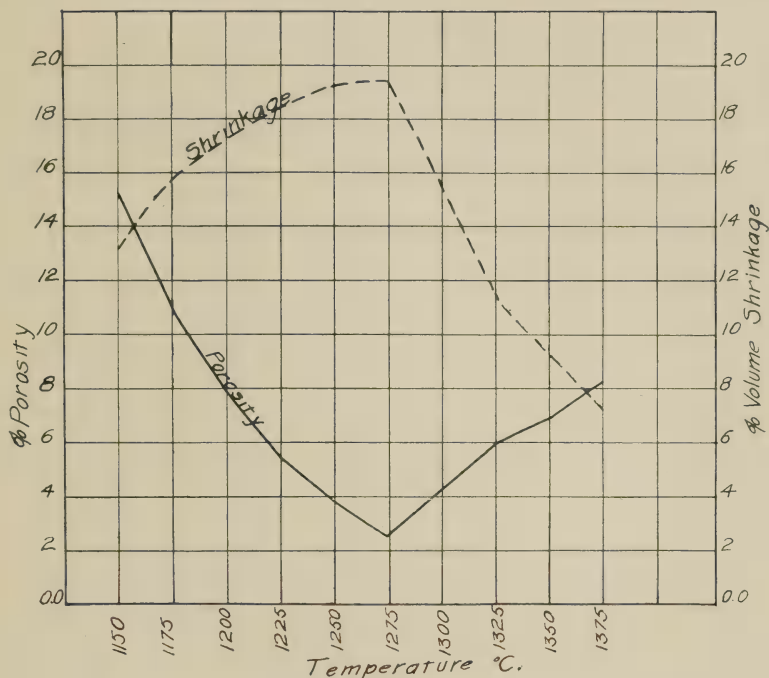


FIG. 4.

3. To the presence or absence of hair cracks—small cracks so often developed by sagger mixtures in drying and burning.

4. The proportion of grog to raw-clay used and the uniformity of mixing and tempering.

1. *Bonding Clays.*—A certain amount of vitrifying bond clay is necessary to the production of a sagger of good mechanical strength in the cold. By the sole use of an open-burning bond clay the particles of grog are held loosely together and weak sagers result. By the use of a vitrifying bond-clay the grog particles are held firmly together. The use of a certain amount of a vitrifying bond-clay having a burning behavior similar to that shown in Fig. 1, is desirable in order to secure a sagger of the desired strength. The greater the amount of vitrifying bond clay used the greater will be the strength of the resultant sagers.

It is not desirable to use too much of the vitrifying clay. In order to secure a sagger of the desired openness a certain amount of open-burning clay, having a burning behavior similar to that shown in Fig. 2, must also be used. By confining our mixture to grog, a vitrifying clay and an open-burning clay, and by varying the proportions of the two clays, we can secure a sagger of any desired mechanical strength in the cold. A good proportion is, say 50 per cent grog, 20 per cent vitrifying clay and 30 per cent open-burning clay.

2. *Sagger Grog*.—It has been our experience that too little attention has been paid to the screening of grog for sagger mixes and that our knowledge of the best practice is limited. The work of F. A. Kirkpatrick¹ on the effect of the size of grog in fire clay bodies has thrown considerable light on this subject. In a sagger mixture in which there is a preponderance of large sized grog particles, the spaces between the grains are filled with the bond clay which, in vitrifying, allows the particles of grog to slide upon each other. Instead of having a skeleton of grog particles touching at many points and held together by the bond clay we have a matrix of bond-clay in which are imbedded the grog particles and the bond-clay becomes the predominating factor in the behavior of the mixture.

The proportions of the sizes of grog particles secured by screening through a single sieve are very irregular—this being especially true if a sieve of large mesh is used. As an illustration, a grog which was prepared by passing through a $\frac{3}{8}$ mesh sieve had the following proportions of different sized grains:

$\frac{3}{8} - \frac{1}{4}$ mesh	36 per cent
4 - 8 mesh	30 per cent
8 - 12 mesh	10 per cent
12 - 20 mesh	9 per cent
20 - 40 mesh	8 per cent
Through a 40 mesh . . .	7 per cent

It will be noted that in this grog the larger particles predominated and very little shaking caused the finer particles to settle out leaving a skeleton of coarse grains.

¹ *Trans. Am. Ceram. Soc.*, **19**, 268-300 (1917).

3. *Hair Cracks*.—We have often observed the small hair cracks in saggars, sometimes present in the green sagger before burning but more often observed in the burned saggars. These hair cracks may be caused by the use of a too large-mesh screen in sieving the grog, to improper proportioning of the grog particles, to the use of a bond clay which has an excessive drying and burning shrinkage, or to a combination of the above causes. If there is a preponderance of large sized grog particles there will be an excess of bond clay between the grog grains, and the bond clay, having a greater shrinkage than the grog, decreases in volume and pulls away from the grog particles causing a strain and producing the small cracks which are bound to decrease the mechanical strength of the sagger. The qualities imparted by coarsely ground grog in the sagger mixture may be more than offset by improper proportioning of the grog grains and the resultant unsound structure produced by the small hair cracks.

The general practice in Europe—employed to a limited extent in this country—of grading the particles of sagger grog into different sizes and then adding definite proportions of each size to the sagger mixture is an excellent one. In this way the voids between the larger sized grog particles are filled with smaller sized grog particles and so on until we have a skeleton of grog particles held together by the bonding clays. A mixture of this kind will have a smaller drying and burning shrinkage and greater mechanical strength when burned than a similar sagger mixture in which there is a preponderance of the larger sized grog particles.

3. **Resistance to Deformation**.—As we have previously stated, failures due to deformation of the saggars appear to be fewer than the losses due to breakage.

The causes of the deformation of fire clay bodies in general and in particular of fire brick have been very thoroughly studied—especially by the Bureau of Standards.¹ We are all more or less familiar with the load test as applied to fire brick when heated to high temperatures. The behavior of a fire brick when weighted down or loaded is analogous to the behavior of a sagger when filled with ware. In the case of the fire brick it has been found that the deformation under a load is largely due to the softening

¹ Bur. Standards, *Tech. Paper* 7.

of the bonding clay used in holding together the particles of grog. A vitrifying clay softens and deforms more readily than an open-burning clay and hence, if our saggars are failing through bending or deformation, the remedy is to use a smaller percentage of vitrifying clay, or to substitute a refractory open-burning clay for some or all of the tight-burning clay used in the sagger mixture.

4. Resistance to Temperature Changes.—A large proportion of sagger breakage appears to take place during the cooling down of the saggars in the kiln. It has been well established that a very dense vitrified fire clay body has less resistance to temperature changes than a fire clay body retaining an open structure after burning. A sagger mix prepared from a dense grog and excessive quantities of vitrifying bond clay is bound to be very sensitive to changes in temperature. The structure of the sagger should be as open and porous as possible without sacrificing its mechanical strength in the cold. This, of course, is governed by a proper proportioning of the contents of open-burning and vitrifying bond clay used in the mixtures.

The cracking and breaking of saggars is undoubtedly in many instances due to the use of open-burning bond clays, having a high content of sand. The practice of adding sand to a sagger mixture is not a sound one from the information which is available. The sensitiveness to cracking of all clay products containing a high percentage of silica is well known.

Silica brick, which contain from 93 to 98 per cent silica, are particularly sensitive to changes in temperature and for this reason are not used in a great many furnaces which are heated up and cooled down intermittently. We have encountered a greater tendency in the so-called quartzite or siliceous refractories to crack and spall than is observed in the so-called high clay refractories. We know that red-burning clays, containing a high percentage of sand, used in some localities in the manufacture of common building brick, are very sensitive to cracking if cooled down quickly in the kilns. By the introduction into a sagger mix of an open burning bond clay having an excess of free sand, we are inviting cracking and breaking of the saggars—through the inability of the sagger as a whole to withstand the volume changes of the particles of sand introduced in the bonding clay.

The irregular thermal expansion and contraction of the different forms of silica is the source of trouble in the manufacture of a great many of our ceramic wares. It has given trouble through the cracking and "dunting" of terra cotta, of vitreous and porcelain sanitary ware, fire brick, and in every clay product in which there is an excess of silica, either in the form of sandy fire-clays or in the form of flint as in our white burning pottery products.

We would, therefore, expect that the introduction of an excessive amount of sandy clay into a sagger mixture is very liable to cause cracking—followed by breaking of the sagger either in the same or in the succeeding burn.

Raw Materials and Composition.

In view of the above, therefore, it is not sufficient that we know the burning behavior of our sagger clays—whether vitrifying or open-burning. We must also know something of their composition, especially as regards their content of coarse or even very fine grained sand or silica. Obviously, the sagger should be as free from iron as possible and from all granular materials which are liable to cause popping or spitting-out.

It is significant that, in the manufacture of ceramic products which are particularly designed to withstand temperature changes and especially of the higher grade wares, it has been found necessary to eliminate silica in the form of flint from the body mixtures. We may mention particularly the porcelain tubes used in insulating the thermocouple wires of pyrometers. The well-known Marquarat¹ tubes are known to have a high content of alumina and little or no free silica was used in the preparation of the body. The same is true of the porcelain pyrometer tubes now being manufactured in this country. Flint has been eliminated from the body and calcined aluminous mixtures have been substituted in its place. Flint has also been found objectionable in the special porcelains which are subjected in use to temperature changes—such as gas-mantle rings, porcelain insulators, etc.

Attention should be called to the use of kaolin in sagger mixtures. In addition to being highly refractory and open burning,

¹ *Trans. Am. Ceram. Soc.*, 18, 268 (1916).

the kaolin does not contain excessive amounts of sand as do the sandy open-burning fire clays. Very satisfactory refractory bodies have been prepared from mixtures of kaolin, vitrifying fire clay and grog. The mixtures have low drying and burning shrinkage, and have great resistance to deformation at kiln temperatures. The use of kaolin, however, is not necessary providing we can secure a clay which retains a high porosity at the firing temperature. Deposits of secondary kaolin occur in this country, which, although they may not be satisfactory for use in the manufacture of high grade pottery, would be very valuable in the manufacture of saggars. We have found that the addition of kaolin in amounts as low as 10 per cent materially improves the refractoriness and other qualities of sagger or other mixes.

The composition of the grog used in a sagger mixture is governed, of course, by the composition of the raw clays used in the mixture, *i. e.*, if the grog is prepared by the crushing of old saggars the addition of a small quantity of kaolin into the mixture tends to maintain the refractoriness of the grog.

. Preparation of the Mixtures.

Although most of our sagger mixtures are prepared by the soaking pit method, we would call attention to some of the advantages of using the ordinary wet-pan in mixing and tempering sagger mixtures. We have found that by the use of a wet-pan a much more uniform mixing of two or more clays is secured than by the use of a soaking-pit. The soaking-pit method depends upon the slaking down of the clays in water. If our sagger clays slake down readily in water the soaking-pit method is not so objectionable. However, we know that some fire clays will remain in water for a long time without slaking down. Clays of this kind should not be used in batches prepared by the soaking-pit method. The writer has seen saggars, made from a mixture of red and buff clay and grog mixed by this method, in which the red and yellow particles of the bond clays used could still be distinguished in the molded sagger. The use of the pug-mill in connection with the soaking pit does not always overcome the objections to the

soaking-pit method of preparation. The heavy mullers of the wet-pan crush the particles of clay and thoroughly blend the two or more clays used in the mixture.

We have also found that by the use of the wet-pan a larger percentage of grog can be introduced into the sagger-mixture without the loss of its necessary working qualities. This is accounted for by the fact that the wet-pan develops the maximum plasticity of the bond clays and hence increases their carrying capacity for grog. The advantage of the increased grog content is the lower shrinkage of the mixtures. Saggings prepared from wet-pan mixes also mold better and with smoother surfaces.

Objections have been raised to the wet-pan method on the grounds that the heavy mullers of the pan crush the larger particles of grog and make it too fine. This objection may be overcome¹ by the use of a wet-pan having mullers which are raised slightly off the bottom of the pan. By the use of a pan of this type, the particles of grog slide underneath the mullers without being crushed.

Summary.

In summarizing, we may say, therefore, that the length of life of saggings is influenced by a great many factors, not the least of these being the necessity of care in the preparation of the mixtures and in the drying and first burning of the completed saggings.

In order to produce a sagger giving maximum service, a thorough knowledge of the composition and burning behavior of the clays used in the sagger mixture is necessary.

DEPARTMENT OF CERAMICS,
RUTGERS COLLEGE.

¹ *J. Am. Ceram. Soc.*, 1, 18 (January, 1918).

MAGNESIA WARE.

BY TRYGVE D. YENSEN.

Readers of Mr. Ferguson's recent note in *THIS JOURNAL*,¹ on the Sintering of Magnesia, might get the impression, quite unintentional on the part of the author, that the world is and has been absolutely dependent upon Germany for magnesia ware. It is true—as far as the writer is aware—that magnesia wares, such as crucibles and tubes of American manufacture, have not thus far been sold in the open market in this country, but it has been produced in considerable quantities in metallurgical laboratories. The process of manufacture—although requiring electrical furnaces of considerable capacity—is quite simple, and has been fully described in the technical literature.

More than ten years ago, Dr. C. F. Burgess, who was then connected with the University of Wisconsin, obtained a patent on a process of manufacturing MgO crucibles, consisting in placing crushed or powdered MgO, previously sintered or fused, in a graphite mold, the inside part of which was split so as to form a heating element through which an electric current could be passed for the purpose of heating the magnesia to a sintering temperature. It is not known whether this process was ever successfully applied. The author has tried forming magnesia crucibles without the use of binders by means of graphite molds heated in an electric furnace to 1800° C. While the product was strong and sound there was strong evidence of reduction of MgO by the graphite of the mold, with the result that the crucible was not uniform and furthermore that the inside of the mold was consumed to such an extent that it could be used only once. It is supposed that similar difficulties were encountered by Dr. Burgess in the application of his patented process. However this may be, magnesia was fused at the University of Wisconsin and the fused MgO crushed and made into magnesia crucibles before 1910.

¹ J. B. Ferguson, "Note on the Sintering of Magnesia," *J. Am. Ceram. Soc.*, 1, 439 (1918).

The work has been continued since that time by Watts,¹ Kowalke and others, and magnesia crucibles have been in common use there.

Since 1912 the author has been making magnesia crucibles for laboratory purposes almost without interruption. A description of the method used was first published in 1914.²

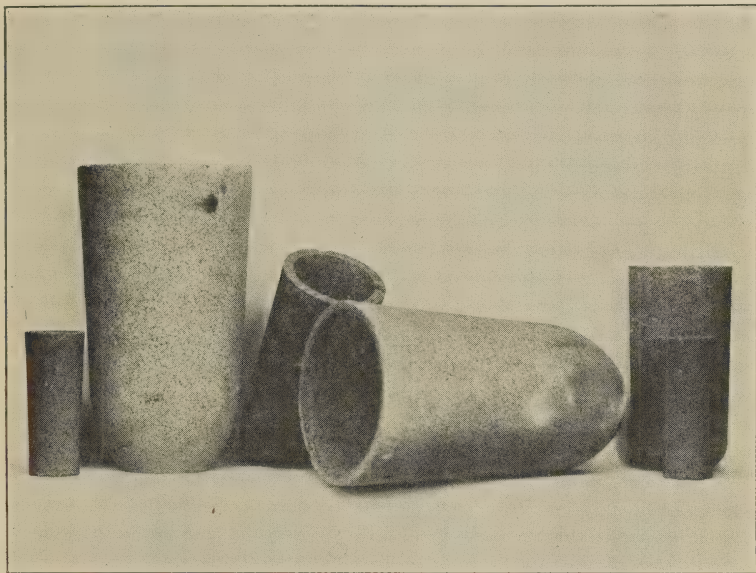


FIG. 1.

Calcined magnesite was fused in an electric arc furnace, the fused MgO crushed to go through a 40-mesh screen, then mixed with about 5 per cent hydrated magnesia, molded into crucibles in a steel mold, dried and finally heated to 1800°C in an electric furnace. The crucibles thus made were uniform, strong, had little shrinkage and showed no sign of softening at 1800° . Chem-

¹ O. P. Watts, "Making Magnesia Crucibles," *Wisconsin Engineer*, **17**, 64 (1913).

² Yensen, "Magnetic and Other Properties of Electrolytic Iron Melted in Vacuo," Eng. Expt. Sta., University of Ill., *Bull.* **72**, appendix 1, 49-51 (1914).

ical analysis showed the finished product to contain about 95 per cent MgO , the remainder being chiefly SiO_2 , Fe_2O_3 and Al_2O_3 . A purer product of still higher refractoriness could be obtained by using a purer material to start with, but for the purposes intended by the author the above amounts of impurities caused no trouble.¹

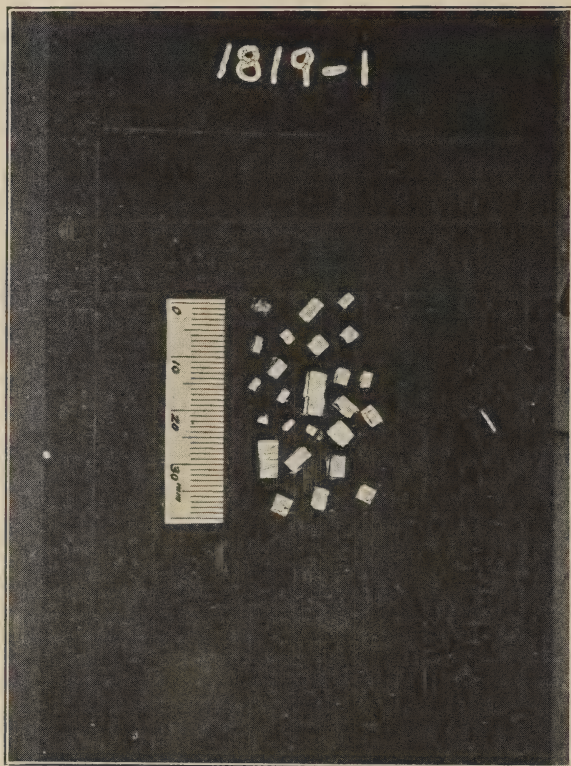


FIG. 2.

During the last two years magnesia crucibles of various sizes have been made in considerable numbers at the Westinghouse Research Laboratory, a description of which was published last year.² A photograph of some of these crucibles is shown in Fig. 1. The method used is essentially the same as that employed at the University of Illinois.

¹ Results published by the Bureau of Standards show that the melting point of pure MgO is 2800°C , Bur. Standards, *Sci. Paper* 212, June, 1913.

² Yensen, "Preparation of Pure Alloys for Magnetic Purposes," *Trans. Am. Electrochem. Soc.*, 32, 176 (1917).

The author has made attempts to persuade manufacturers of refractories to take up the manufacture of magnesia ware such as crucibles and tubes, but thus far without success. It seems as though the manufacturers are not yet convinced that there is a sufficient market for this kind of ware to warrant going into the business, and yet there is no product on the market today that can be used as a successful substitute for it as a container for the purpose of melting pure iron and iron alloys. Until some progressive manufacturer can be persuaded to hazard the undertaking, it seems therefore probable that each individual user will have to manufacture his own magnesia crucibles.

It has recently been brought to the author's attention that crystals of MgO may be of value for certain optical purposes. Large crystals were separated from pieces of fused MgO and examined by Dr. P. G. Nutting who found these crystals to be cubical and isotropic and to have very high refractive index and low dispersion—properties that indicate valuable lens material. This phase of fused magnesia has been described in detail by Dr. Nutting at the Baltimore Meeting of the Optical Society, December 27th. A photograph of some of the crystals is shown in Fig. 2.

RESEARCH LABORATORY,
WESTINGHOUSE ELEC. & MFG. CO.,
EAST PITTSBURGH, PA.

ACTIVITIES OF THE SOCIETY.

Action by the Board of Trustees.

The motions listed on page 587 of the JOURNAL as pending have been passed by the Board without further amendment, except in the case of motions 3 and 5 in the list proposed by the President. These have been amended and passed in the following form:

3. "That, as of the date of November 1, 1918, fifty (50) copies of each volume of the Transactions be reserved for sale in complete sets only, and that the Secretary be instructed to purchase at five dollars (\$5) each, sufficient copies to bring the total stock of each volume to that figure. It is the sense of this resolution that a complete set shall mean nineteen Volumes, Nos. 1 to 19, inclusive, of the "Transactions of the American Ceramic Society."

5. "That copies of the volumes of Transactions and of the Journal shall be furnished to members who have or shall allow their dues to become delinquent only after the number reserved for sale has been provided. Furthermore, that in cases in which the volume that should be furnished in consideration of a certain year's dues is not available, the member shall have the option of selecting any available volume, or paying only the difference between his annual dues and the price to members of the Volume or the subscription price of the JOURNAL to members.

ACQUISITION OF NEW MEMBERS DURING DECEMBER, 1918.

Associate.

Dr. P. G. H. Boswell, The University, Liverpool, England.

S. Paul Ward, Rancagua, Chile, South America.

J. S. Laird, University of Michigan, Ann Arbor, Michigan.

Harry W. Fenton, Akron Smoking Pipe Co., Mogadore, Ohio.

J. E. McAllister, J. L. Mott Co., Trenton, N. J.
Frank E. Lauer, 2389 Mance St., Montreal, Canada.
J. P. Callaghan, Sharon Clay Products Co., Sharon, Pa.
C. B. Young, Ohio State Brick & Stone Co., Newark, Ohio.
Maurice A. Smith, McKee Glass Co., Jeanette, Pa.
Harry A. Truby, Pittsburgh Plate Glass Co., Creighton, Pa.
H. Homer Knowles, Box 427, East Liverpool, Ohio.
Fenwick D. Foley, St. John, N. B.
Paul R. Morris, 300 East 9th Ave., Tarentum, Pa.
N. B. Radabaugh, 1572 Rydal Mt. Rd., Cleveland, Ohio.

LOCAL SECTION MEETINGS.

NEW ENGLAND SECTION.

Boston, Mass., January 11, 1919.

The meeting was called to order by Chairman A. A. Klein at the Boston City Club, at 7 P.M., with twenty members present.

Mr. Klein spoke of the recent death of Mr. C. L. Walduck and his loss to the Society. It was voted that a committee be appointed by the chair to draw up resolutions and that copies be sent to his parents and to the American Ceramic Society.

Later in the evening the committee reported as follows:

"We, members and appointed representatives of the New England Section of the American Ceramic Society, in remembrance of the sterling qualities of Charles L. Walduck personally and his efficient services as Secretary of this Section, wish to record our much felt loss of him as a man and as Secretary of this Section. We extend our sympathies to his parents and recommend to our parent organization, the American Ceramic Society, a suitable obituary notice in their JOURNAL."

W. G. Whitmore,
R. C. Purdy,
M. F. Cunningham.

The officers elected for the coming year were:

Chairman, W. H. Grueby, Grueby Faience & Tile Co., Boston, Mass.; *Secretary and Treasurer*, Charles J. Hudson, Norton Co., Worcester, Mass.; *Councilor*, Charles H. Kerr, American Optical Co., Southbridge, Mass.

Mr. R. C. Purdy spoke interestingly on the purpose of the Section both as regards itself and its relation to the American Ceramic Society. Two interesting and valuable talks followed:

"Some Problems of the Glass Manufacturer," by C. H. Kerr of the American Optical Company and "Clay Testing Methods and Purposes," by Carl H. Lawson of the Norton Company, Worcester, Mass. A general discussion of the papers followed.

During the afternoon previous to the meeting the members enjoyed a trip through the chemical laboratories of Arthur D. Little, Inc.

Charles J. Hudson, *Secretary*.

PITTSBURGH DISTRICT SECTION.

At a meeting held at the Mellon Institute, University of Pittsburgh, Pittsburgh, Pa., December 19, 1918, the merging of the former Beaver Section into the Pittsburgh District Section was completed. Morning and afternoon sessions were held.

At the opening of the morning session by-laws were adopted and the following officers were elected for the ensuing year: R. R. Hice, *Chairman*, C. R. Peregrine, *Vice-Chairman*, Thos. H. Sant, *Treasurer*, F. H. Riddle, *Secretary* and F. W. Walker, Sr., *Councilor*.

After the election of officers a varied and interesting program of technical papers was afforded as follows:

"Industrial Research," Dr. E. W. Tillotson, Mellon Institute.

"The Effect of Some Fluxes on Porcelain," F. H. Riddle, Bureau of Standards.

"The Influence of Some Ball Clays upon the Casting of Clay Wares," J. W. Wright, Bureau of Standards.

"The Hydraulic Properties of the Calcium Aluminates," P. H. Bates, Bureau of Standards.

"Note on the Electrical Resistance of Porcelains at Temperatures up to 800° C," A. V. Bleining, Bureau of Standards.

Members desiring to become affiliated with the above Section should communicate with the Secretary, F. H. Riddle, Bureau of Standards, 40th and Butler Sts., Pittsburgh, Pa.

JOURNAL

OF THE

AMERICAN CERAMIC SOCIETY

A monthly journal devoted to the arts and sciences related to the silicate industries.

Vol. 1

November, 1918

No. 11

EDITORIALS.

GROWTH OF THE SOCIETY.

The American Ceramic Society has been in existence twenty years. During that time it has grown in membership from 22 to nearly 1100. The Society represents industries, the value of whose output—including clay products, glass and cement—aggregates \$450,000,000 annually in the United States. The Society seeks to occupy towards the clay, glass and cement industries the same position of leadership that the American Chemical Society, the American Society of Civil Engineers, the American Society of Mechanical Engineers, the American Institute of Mining Engineers, and some others, occupy in their respective fields. The 100 per cent increase in membership of the Society during the past two years indicates the need of an organization of its kind and augurs well for the future welfare and growth of the Society.

The Society should, however, profit by the experience and example of other technical organizations and endeavor to co-ordinate its activities through permanent officials, having no other business in life than the advancement of the Society's interests. With the steady growth in membership and the widening and intensification of its activities through the Journal, Local Sections, Professional Divisions, etc., the Society's business is becoming too large and varied to depend upon the part time services of its committees and executive officers. With the in-

creased revenue through the accession of new members and the gratifying support from firms and corporations through contributing memberships, the time is fast approaching when the Society will be fully able to financially support the coördination of its activities through full-time executive officers. Let us lend our efforts in this direction!

KILNS.

There is no problem of more importance facing the manufacturer of ceramic products than that of the selection of the type of kiln best suited for the burning of his wares. The low efficiency of the average periodic kiln renders it the greatest source of economic loss in most of the plants where used. The rising cost of fuel and the necessity of its conservation in the future render the kiln question an increasingly vital one.

The discussions in recent numbers of this and other Journals as to the efficiencies and applicability of the available types of kilns to the burning of the different kinds of ceramic products leave the selection in most cases a wide open one, and a verdict has not as yet been reached. The question recently raised in the editorial columns of a contemporary Journal as to the design and efficiency of the modern by-product coke ovens should give ceramic engineers and manufacturers serious food for reflection. Have we arrived at the millennium in kilns or will the future produce radical types far superior to any which have been placed upon the market thus far? It is doubtless true that no one type of kiln will be developed which will be applicable to the burning of all grades of ceramic wares.

The suggestion that at the next annual meeting of the Society there be a symposium on kilns should receive attention at once. At that time the presentation of reliable data as to the relative efficiencies of the different types of kilns now in use and also unbiased reports as to the service rendered will be a step forward in the solution of this vexing problem. In the meantime, there is need for more data as to the efficiencies of present installations, and it is to be hoped that ceramic engineers will continue to collect and make data of this kind available.

ORIGINAL PAPERS AND DISCUSSIONS.

A CONTRIBUTION TO THE METHODS OF GLASS ANALYSIS, WITH SPECIAL REFERENCE TO BORIC ACID AND THE TWO OXIDES OF ARSENIC.

BY E. T. ALLEN AND E. G. ZIES.

In the course of the work on optical glass undertaken by the Geophysical Laboratory in the year 1917-18 some investigation was made of the well-known Jena optical glasses. It included among other things complete chemical analyses of a considerable number of them, to determine the composition in doubtful cases and to see if anything could be learned respecting the relation of composition to quality. In this connection the authors spent considerable time in testing the accuracy of certain analytical methods and in devising others, an account of which is here given.

We had supposed that the system of silicate analysis so well worked out for rocks by Hillebrand and others could be applied with little or no change to glasses. But glasses contain certain elements like boron and arsenic seldom found in rocks in appreciable quantities; many such elements, in fact, if all sorts of glass are considered. Again, glasses contain certain combinations of elements which are difficult to separate and determine accurately by ordinary methods. On the whole we have found them considerably more difficult to analyze than rocks.

E. C. Sullivan and W. C. Taylor have realized these difficulties and have made valuable contributions to the subject,¹ especially along the line of rapid analytical methods. Our work may supplement theirs in some measure. We have devoted our attention

¹ *J. Ind. Eng. Chem.*, 6, 897 (1914).

for the most part to optical glasses, and our chief purpose has been to improve the accuracy of the methods. At the same time in the work done on boric acid and the two oxides of arsenic we have also kept in mind the more general utility of the methods.

I. Determination of Trivalent and Pentavalent Arsenic.

It may be confessed at the outset that the time and space devoted in this paper to the determination of arsenic will probably seem entirely disproportionate to the rest of the subject. The chief reason for the more detailed study of this determination was our interest in the role which arsenic plays in glass making. The percentage of arsenic in glasses is so small that if we are to follow successfully its history from the batch to the finished glass we must have an unusually accurate method for its determination. When later it became evident from our work that Gooch and Browning's very accurate iodometric method for arsenic acid could be applied to the determination of arsenic in all substances where it could first be accurately transformed into the sulphide, we felt further justified in the course we had followed.

Glass commonly, but not invariably, contains arsenic. All the Jena optical glasses which we have examined contain it. The total arsenic in glass may be directly determined by fusing a weighed portion with alkali carbonate and nitrate, removing any nitric acid which remains by evaporating to dryness with sulphuric acid, filtering off the silica and insoluble sulphate, if any, and precipitating the arsenic as sulphide; this may finally be transformed into magnesium pyroarsenate and weighed, or reduced by hydriodic acid and titrated with standard iodine solution.

When a mixture of arsenic acid and arsenious acid is evaporated in platinum with hydrofluoric and sulphuric acids, the arsenious acid is completely volatilized as the trifluoride, while all the arsenic acid remains in the residue entirely unreduced. Thus the two oxides are very accurately separated from one another; the pentavalent arsenic may be determined in the residue and the trivalent arsenic by difference between the pentavalent and total arsenic. The trivalent arsenic can also be *directly* determined in the distillate if the operation is carried out in a gold or platinum still of suitable form.

1. Determination of Total Arsenic.—There is no element of originality in this determination; we have simply proved by synthetic experiments that no arsenic is lost in a fusion with sodium carbonate and niter, and that fairly satisfactory estimations of the total arsenic in glass may be made after separating the arsenic as sulphide, oxidizing the latter with hydrogen peroxide and ammonia, precipitating the arsenic from this solution as magnesium ammonium arsenate and finally weighing it as pyroarsenate. Further, if the solution formed by oxidation with hydrogen dioxide and ammonia is reduced by hydriodic acid and titrated by a standard iodine solution, after the method of Gooch and Browning, the determination becomes highly accurate and may be done in far less time.

Volatilization of Arsenic in the Process of Fusion Involved in Analysis.—Unfortunately for the purposes of analytical control it is not possible to prepare a glass which shall contain a given amount of arsenic trioxide and probably not possible to prepare one carrying a given amount of arsenic pentoxide. The possible loss of arsenic by volatilization during the fusion with sodium carbonate which is involved in the decomposition of a glass for analysis, had therefore to be tested indirectly. To this end we took mixtures of arsenious oxide in known quantity and a powdered glass containing no arsenic. To these were added 3 g. pure dry sodium carbonate per gram of glass, the fusion was made as in an ordinary determination of silica and the arsenic was determined in the product. An appreciable quantity of arsenic was lost.

Taken.....	0.0530 g. As_2O_3
Found 0.0797 g. $\text{Mg}_2\text{As}_2\text{O}_7$ equivalent to..	0.0508 g. As_2O_3
<hr/>	
Loss.....	0.0022 g. As_2O_3

In a second experiment:

Taken.....	0.0710 g. As_2C_3
Found 0.1058 g. $\text{Mg}_2\text{As}_2\text{O}_7$ equivalent to...	0.0674 g. As_2O_3
<hr/>	
Loss.....	0.0036 g. As_2O_3

When a small amount of niter, about 0.1 g., was added to the

flux a still greater quantity of arsenic trioxide was fused *without* loss.

Taken.....	0.1010 g. As_2O_3
Found 0.1589 g. $\text{Mg}_2\text{As}_2\text{O}_7$ equivalent to.	0.1013 g. As_2O_3
.....	0.0003 g. As_2O_3

The determination of the arsenic was made as outlined above and described in detail further on. Now, although it is quite possible that *arsenic which is combined in a glass* might be entirely retained when the glass was fused with sodium carbonate *alone*, it is undoubtedly safer to add niter, for the carbonate sometimes contains bits of organic matter, possibly paper or cardboard, which would almost certainly lead to the volatilization of metallic arsenic during the fusion of the glass. Convenient details for the method follow:

Fuse 1 g. of powdered glass with 3 g. pure, dry sodium carbonate and about 0.1 g. potassium nitrate. When cool, set the crucible in a 12 cm. casserole, add water, cover and put in 10 cc. 1 : 1 sulphuric acid.¹ Warm until the fusion cake is removed, clean and remove the crucible and evaporate till white fumes appear. Heat somewhat longer until the silica becomes dense enough to filter without trouble; cool, add hot water and boil till any insoluble sulphate settles satisfactorily. Barium gives trouble here, because in evaporating to dryness the sulphate is partially redissolved in the concentrated sulphuric acid and is again precipitated in a fine state of division by the addition of water. Filter with suction, wash a few times with boiling water and *suck dry*. The filtrate may be kept down to 100 cc. For fear the bulky precipitate may retain a little arsenic, open the filter and transfer the precipitate to a 20 cc. platinum crucible with the aid of a stout platinum wire, add a little sulphuric acid and 5 cc. hydrofluoric acid and evaporate to white fumes. Cool, transfer the residue to a small beaker with a little hot water, boil and filter, adding the filtrate to the principal one. To the filtrate from silica add a fragment of potassium iodide, heat and

¹ Hydrochloric acid cannot be used here because, as is well known, arsenious acid is thus volatilized as the trichloride, and even arsenic acid is partially reduced and volatilized.

precipitate the arsenic with hydrogen sulphide. The precipitation is materially accelerated by the reduction of the arsenic acid by hydriodic acid. When the precipitate has well coagulated, cool partially in order that the solution may absorb some excess of hydrogen sulphide, stopper and set aside. If the solution is filtered immediately the results are likely to be too low.

Experiments were made on the precipitation of the arsenic from a strong hydrochloric acid solution, *without previous separation of silica*, but so much silica came down with the sulphide causing so much subsequent trouble that this method was abandoned.

Of course if antimony is present it will have to be separated from the arsenic by one of the regular methods. If the glass contains lead, the precipitate will generally have an orange color, but the color is due to the presence of a little sulphide of lead. If the sulphate solution is allowed to stand before treatment with hydrogen sulphide till the lead is completely precipitated the sulphide precipitate is a clear yellow. The addition of arsenic and antimony together has been tried in glass making, but all the glasses we have examined contained either one or the other but not both. After standing overnight, the arsenic sulphide is filtered and washed with hot water acidulated with sulphuric acid.

The sulphide is then treated on the filter with a few cc. of strong ammonium hydroxide, and the flask rinsed with the same. The filter is washed two or three times with a few cc. of hot water. If it shows any residue after the solution of the arsenic it is transferred to a 150 cc. beaker and digested warm with ammonia and a little ammonium carbonate. The orange precipitates mentioned above have to be digested a short time before they show the dark brown color of lead sulphide, and the suspicion is that till then they still retain arsenic. The soluble portion is added to the principal arsenic solution, which is conveniently handled in a 250 cc. beaker, and oxidized by hydrogen peroxide—3 to 5 cc. of a 3 per cent solution is sufficient. Cover the beaker and boil for some time on the hot plate to complete the oxidation and decompose the excess of peroxide. We have confirmed the statement in the textbooks that a complete oxidation is accomplished in this way

Levol's Method¹ for the Determination of Arsenic.—If the arsenic is to be determined gravimetrically, the solution is now precipitated with magnesia mixture, the precipitate is washed, dried at 130° and then slowly heated in the electric oven to 550° where it appears to be stable. The precipitate gains again on the balance (1 to 2 mg. in the case of a large precipitate), and the final weight agrees best with the quantity of arsenic taken, though this may be due to a compensation of errors. Our results by this method on pure arsenic solutions were satisfactory, as the sequel shows, but the results on glasses did not show the accuracy which our ultimate purpose required. (See p. 760.) It will be remembered that one cannot control his results by working with a synthetic glass containing a known quantity of arsenic; he must depend on the agreement of duplicate determinations and the comparison of different methods. The following table shows the agreement of results which one may obtain when the Levol method is applied to the determination of arsenic in glasses.

TABLE I.

Total arsenic in some Jena optical glasses determined as $\text{Mg}_2\text{As}_2\text{O}_7$, showing the agreement of duplicates. Results in milligrams per gram of glass.

No.	1	2	3	4	5	6	8	9	11	15
Kind of glass. *Schott's numbers.	O3832	O340	O154	O144	O167	O211	O2071	O1209	O722	O599
$\text{Mg}_2\text{As}_2\text{O}_7$	7.0 5.8	5.2 6.5	2.9 2.7	3.9 4.0	3.4 3.6	6.1 7.2	7.1 8.3	5.5 6.2	7.2 8.1	3.7 4.1
Mean	6.4	5.8	2.8	4.0	3.5	6.6	7.7	5.8	7.7	3.9
Equivalent to As_2O_5	5.2 4.3	3.9 4.8	2.1 2.0	2.9 3.0	2.5 2.7	4.5 5.3	5.2 6.2	4.1 4.6	5.3 6.0	2.7 3.0
Mean	4.8	4.3	2.0	3.0	2.6	4.9	5.7	4.4	5.7	2.9
Variation in As_2O_5	0.9	0.9	0.1	0.1	0.2	0.8	1.0	0.5	0.7	0.3

* See Doelter's "Handbuch der Mineralchemie," Bd. I, 6, pp. 871-889, for the approximate composition of some of these glasses.

¹ See especially Levol, *Ann. chim. phys.*, [3] 17, 501; Austin, *Am. Jour. Sci.*, [4] 9, 55 (1900).

The method may serve very satisfactorily for large quantities of arsenic, but for these small amounts the percentage error is inadmissibly high. As the Levöl method is the handiest method for the determination of arsenic where only occasional results are required, we spent some time in the effort to increase its accuracy.

When the results in Table 1 are compared with those obtained later by the Gooch and Browning method (see Table 3) a number of them are found to be considerably too high. Several magnesium ammonium arsenate precipitates obtained in the analysis of glasses were examined for insoluble matter like silica, lead sulphate or barium sulphate, but solution in a few drops of warm dilute hydrochloric acid failed to reveal any. When the filter and residue were incinerated, never over 0.2 mg. was found.

The only possible clue to the high results which we have is one abnormally high determination obtained by precipitating magnesium ammonium arsenate in the presence of considerable hydrogen peroxide.

Taken.	Found.
As ₂ O ₅ ... 0.0116 g.	Mg ₂ As ₂ O ₇ 0.0392 g.
H ₂ O ₂ ... 5 cc. 3 per cent solution	As ₂ O ₅ 0.0290
Total volume about 25 cc.	

We do not know the meaning of this result, but if hydrogen peroxide can cause too high results in the precipitation of arsenic by magnesia mixture, some of our errors in the determination of arsenic by the Levöl method may have been due to the incomplete removal of hydrogen peroxide from the solution after the oxidation of the arsenic.

Further work on this line was abandoned when we had tested the volumetric method described below.

Method of Gooch and Browning.—Much more accurate than the Levöl method is the method of Gooch and Browning¹ according to which the arsenic acid is reduced by hydriodic acid to arsenious acid which is then titrated with a standard solution

¹ *Am. Jour. Sci.*, 3, 40, 66 (1890).

of iodine in the usual way. Gooch and Browning worked only with pure solutions of arsenic acid, so that we were obliged to test the applicability of the method to solutions formed by the oxidation of arsenic sulphide with hydrogen peroxide and ammonia.

For these and subsequent tests we used a standard solution of arsenic acid made as follows: First a sample of arsenious oxide was selected from several in stock on the basis of microscopic examination. The sample selected was practically homogeneous showing no intermixture of a higher refracting substance suggestive of the presence of antimony, as some others did. For this examination the authors are indebted to Dr. H. E. Merwin whose experience in such work is quite exceptional. Solution of a portion of the sample in hydrochloric acid showed no residue of sulphide. This sample was sublimed at low temperature several times, only the first fraction in each sublimation being retained. The powdered product was then dried over calcium chloride. For some work it may be that a more rigorous criterion of purity would be required, but the experiments which follow show this preparation to have been quite pure enough for our purposes.

1.0003 g. of this preparation of As_2O_3 was put into a platinum dish and covered with a watch-glass. Concentrated nitric acid was added and evaporated on the water bath, the operation being once repeated. Finally the temperature was carried to about 200° on the electric hot plate and held there till the fumes of nitric acid could no longer be detected. The arsenic acid was dissolved and made up to 100 cc.

10 cc. of this solution was precipitated and determined as $\text{Mg}_2\text{As}_2\text{O}_7$.

Taken 0.1000 g. As_2O_3 equivalent to	0.1161 g. As_2O_5
Found 0.1569 g. $\text{Mg}_2\text{As}_2\text{O}_7$ equivalent to	0.1161 g. As_2O_5

The solution was prepared and evaluated before the adoption of the Gooch and Browning method. For some of the tests another more dilute solution was made in the same way from the same sample of arsenic trioxide. Measured volumes of the standard solution of arsenic acid were diluted with water and made

decidedly acid, 5 cc. 1 : 1 H_2SO_4 to 100 cc. total volume, a little potassium iodide was added and the arsenic was precipitated by hydrogen sulphide. The washing and oxidation of the sulphide have already been described. When, in the course of the oxidation, the ammonia has been expelled and the solution has been reduced to 10 or 15 cc. by evaporation on the hot plate, about 7 cc. 1 : 1 H_2SO_4 is added and the boiling continued about fifteen minutes. Some oxidizing agent¹ formed by the hydrogen dioxide, doubtless a mixture of nitrite and nitrate, is thus removed. If sulphur or sulphide of arsenic is precipitated when the acid is added, the oxidation is of course incomplete. The Gooch and Browning method is carried out advantageously as follows: Pour the oxidized solution into a 300 cc. Erlenmeyer flask marked with a "glass" pencil at the levels to which 40 cc. and 100 cc. of liquid fill it. Dilute the solution to the 100 cc. mark with hot water and add a fragment of potassium iodide—0.3 g. is sufficient for small quantities of arsenic. The two-bulb trap used by Gooch and Browning is set into the neck of the flask, and the liberated iodine is expelled by vigorous boiling. A stream of carbon dioxide led in through a capillary tube prevents bumping and aids in driving out the iodine which the solution retains tenaciously. Gooch and Browning evaporate to 40 cc. and then remove the iodine which remains by rapid addition of very dilute sulphurous acid in required quantity. We regard it as a little more accurate to remove the iodine *entirely* by repeated boiling. To this end add another portion of water (25 cc.), also another fragment of potassium iodide to insure complete reduction, and boil down again to 40 cc., repeating the operation till the solution is colorless. Then dilute quickly with cold water to 75 or 100 cc. and complete the cooling by whirling the flask in a vessel of ice water. Pour in 12 to 14 cc. of a "saturated" solution of potassium carbonate, which has the advantage over sodium carbonate of greater solubility. This neutralizes the major part, but must not neutralize all, of the sulphuric acid. The neutralization is completed by solid sodium bicarbonate. Add starch paste and titrate. It is not well to cool the solution

¹ Ilosvay de Nagy Ilosva, *Ber.*, **28**, 2031 (1895); *Bull. Soc. Paris*, **3**, 2, 351 (1889).

below, say, about 20° or 25° since the speed of the reaction with iodine is then considerably retarded. We use a solution containing about 1.1 g. iodine per liter of solution, so that 1 g. of solution is equivalent to about 0.5 mg. As_2O_5 . The standard solution is

TABLE 2.

Showing the accuracy of the arsenic determination by the iodometric method when the arsenic is first precipitated as sulphide, oxidized by H_2O_2 , reduced, and titrated.

	1.	2.	3.	4.	5.
Grams iodine solution required.....	4.71 ¹	7.85 ¹	11.82 ²	23.30 ²	57.95 ²
Equivalent to mg. As_2O_5	2.1	3.5	5.8	11.5	28.6
Mg. As_2O_5 taken.....	2.3	3.5	5.8	11.6	29.0
Error.....	0.2	0.0	0.0	0.1	0.4

weighed in a weight burette.³ The very satisfactory results in Table 2 show that the Gooch and Browning method for arsenic may be made general, or at any rate that it may be used in all cases where the arsenic can be previously transformed into the sulphide without loss.

The method was now applied to the determination of total arsenic in a series of glasses. The process was that described on page 742, except that the arsenic acid was reduced and titrated with iodine instead of being weighed as pyroarsenate of magnesium. The results appear in Table 3. In these 14 pairs of duplicate determinations, in each of which 1 g. of glass was used, the maximum variation is 0.3 mg. and the mean variation only 0.1 mg. The method is to be commended for its speed as well as its accuracy.

¹ 1 g. of this solution was equivalent to 0.000446 g. As_2O_5 .

² 1 g. of this solution was equivalent to 0.000494 g. As_2O_5 .

³ For improvements in the iodometric method for arsenious acid, see E. W. Washburn, *J. Am. Chem. Soc.*, 30, 31 (1908).

TABLE 3.

Total arsenic in glasses determined iodometrically, in duplicate. As_2O_5 in milligrams per gram of glass.¹

No. of glass.	Kind of glass.	G. iodine solution used.	Mg. As_2O_5 found.	No. of glass.	Kind of glass.	G. iodine solution used.	Mg. As_2O_5 found.
1.....	{ Jena O3832	7.12 7.14	3.2 3.2	9..	{ Jena O1209	11.48 11.58	5.1 5.1
2.....	{ Jena O340	6.34 6.04	2.8 2.7	11..	{ Jena O722	13.74 14.25	6.1 6.3
4.....	{ Jena O144	6.58 6.50	2.9 2.9	13..	{ Jena O578	10.82 10.03	5.3 5.0
5.....	{ Jena O167	7.24 6.49	3.2 2.9	15..	{ Jena O599	6.10 6.17	3.0 3.0
6.....	{ Jena O211	7.60 7.05	3.4 3.1	20..	{ P. P. G. Co. Spectacle Crown	21.71 21.58	10.7 10.7
7.....	{ Jena O2122	11.95 11.94	5.3 5.3	21..	{ P. P. G. Co. Green Plate	5.61 5.62	2.8 2.8
8.....	{ Jena O2071	13.20 13.32	5.9 5.9	22..	{ P. P. G. Co. Dense Flint	19.71 19.56	9.7 9.7

The Separation of Trivalent from Pentavalent Arsenic² and the Determination of Each.—The separation of the two forms of arsenic can be accurately made by heating the mixture in platinum with hydrofluoric and sulphuric acids. The arsenious acid is changed into the trifluoride which is easily and completely volatilized, while *all* the arsenic acid remains in the residue. The operation is conveniently carried out by heating the material in a capacious and loosely covered platinum crucible or small dish by means of an electric hot plate to a final maximum temperature of about 200°. We used crucibles holding 40 or 60 cc. and raised the lid slightly by setting a piece of heavy platinum

¹ In determinations 1–11, inclusive, iodine sol. I was used; 1 g. solution equivalent to 0.000446 g. As_2O_5 . In determinations 13–22, inclusive, iodine sol. III was used; 1 g. solution equivalent to 0.000494 g. As_2O_5 .

² This separation has not been worked out for mixtures which contain antimony.

wire across the top of the crucible. Bumping was prevented by dropping a piece of crumpled platinum foil into the crucible along with the contents and evaporation was accelerated by surrounding the crucible by a fire-clay cylinder.

Standard solutions of arsenious and arsenic acids were used in this series of experiments. The preparation of the standard solution of arsenic acid has already been described (see p. 746). The arsenious solution was made by dissolving a weighed portion of As_2O_3 in a little warm caustic soda solution, diluting sufficiently and acidifying with dilute sulphuric acid. The solution was then cooled and made up to a given volume. 10 cc. arsenious solution containing 0.1000 g. Ag_2O_3 was mixed with 1-2 cc. 1 : 1 H_2SO_4 and 5 cc. HF and evaporated on the hot plate to white fumes. The residue was cooled, diluted with water, neutralized by sodium bicarbonate and tested with starch paste and dilute iodine solution; the first drop struck a blue color. The solution was now acidified with hydrochloric acid, made alkaline with ammonia and tested with magnesia mixture. No precipitate was obtained.

Again 10 cc. of the same arsenious solution was treated in the same way. This time the residue was dissolved in water and tested with hydrogen sulphide. No arsenic was found. All trivalent arsenic is therefore volatilized by heating a substance containing it with hydrofluoric acid in the manner described.

5 cc. of the *arsenic acid* containing 0.0585 g. As_2O_5 was now treated with sulphuric and hydrofluoric acids in a similar manner. The residue was dissolved in water and precipitated by magnesia mixture.

Taken.....	0.0585 g. As_2O_5
Found 0.0791 g. $\text{Mg}_2\text{As}_2\text{O}_7$ equivalent to....	0.0581 g. As_2O_5
Error.....	0.0004 g. As_2O_5

This shows that arsenic acid is not reduced or volatilized by hydrofluoric and sulphuric acids.

When the pure arsenious solution is evaporated on the hot plate to white fumes (max. temp. about 200°) with *sulphuric acid alone* no arsenic is volatilized.

Taken.....	0.1000 g. As_2O_5
Found 0.1562 g. $\text{Mg}_2\text{As}_2\text{O}_7$ g. equivalent to.	0.0995 g. As_2O_5
Error.....	0.0005 g. As_2O_5

In Table 4 (page 752), mixtures of the two standard solutions were used, and to test at the same time the validity of the method for glasses, 1 g. (or in determinations 6 and 7 for lack of material, 0.5 g.) of powdered glass free from arsenic was added to the mixture. In determinations 6 and 7 a flint glass containing 45 per cent lead oxide was used. These results, like those immediately preceding, were done before the method of Gooch and Browning was adopted; hence the arsenic was weighed as magnesium pyroarsenate. They show in a convincing way that the method suffices for an accurate separation of the two oxides of arsenic while the presence of powdered optical glass in no way interferes with it. Also the conditions under which the determinations are made so nearly simulate those of a determination of the arsenic in glass that one can hardly question that the method will suffice to determine the two forms of arsenic in a glass—at least an optical glass where substances which might possibly interfere with the process, such as iron and chlorine, are present in minimum quantity.

S. R. Scholes¹ believed he had determined both oxides of arsenic in glass, in the following way: A weighed portion of glass was dissolved in *hydrofluoric acid and then evaporated with sulphuric acid till the hydrofluoric acid was driven out*. In this solution he reduced the arsenic acid by hydriodic acid and titrated the liberated iodine in the acid solution with standard thiosulphate. He then made the solution alkaline with sodium bicarbonate and titrated the total arsenic with standard iodine. We now know that the solution he used could not have contained any of the arsenious oxide and that his small differences were only the variations between two methods in both of which the arsenic pentoxide and *only* that was actually determined.

Pentavalent Arsenic in Glass.—The above method of separating the two forms of arsenic was now applied to the glasses in

¹ *J. Ind. Eng. Chem.*, 4, 16 (1912).

TABLE 4.

Showing the separation of given quantities of trivalent from pentavalent arsenic and the determination of the latter.¹

	1.	2.	3.	4.	5.	6.	7.
	g.	g.	g.	g.	g.	g.	g.
As ₂ O ₃ taken.....	0.0100	0.1000	0.0100	0.0500	0.0100	None	None
As ₂ O ₅ taken.....	0.0023	0.0058	0.0116	0.0581	0.1161	0.0058	0.0035
Mg ₂ As ₂ O ₇ found.....	0.0032	0.0075	0.0152	0.0777	0.1565	0.0069	0.0052
Equivalent to As ₂ O ₅	0.0024	0.0055	0.0113	0.0575	0.1158	0.0051	0.0038
Variation from As ₂ O ₅ taken.....	0.0001	0.0003	0.0003	0.0006	0.0003	0.0007	0.0003

Table 3 and the pentavalent arsenic was determined in each by the Gooch and Browning method. The results are recorded in Table 5. Duplicate determinations show a maximum variation of 0.3 mg. and a mean variation of 0.1 mg. just as in the determinations of total arsenic. In Table 6 are tabulated the amount of arsenic pentoxide in each glass, together with the amount of arsenic trioxide found by difference between the pentavalent and the total arsenic. Evidently the major part of the arsenic is in the form of pentoxide, indeed the trioxide is so small, ranging from zero to a maximum of 0.09 per cent of the glass, that one is inclined to suspect some systematic and tolerably constant error between the two methods. It seemed quite improbable that errors of this degree of constancy could be caused by spattering on the hot plate during the solution of the glass. Still some losses in the beginning of the work, when fewer precautions were taken, were traced to this source. Before going further, therefore, it was proved beyond question that the results were affected by no such errors.

Effect of the Presence of Ferrous Iron in the Separation of the Two Forms of Arsenic.—It occurred to us that the small differences found between the total and pentavalent arsenic in glasses might be due to the reducing action of ferrous iron. All glasses contain a small amount of iron some of which may be ferrous. Now if this should reduce a little of the pentavalent

¹ Determined as Mg₂As₂O₇.

TABLE 5.

Pentavalent arsenic in glasses determined iodometrically in duplicate.
 As_2O_5 in milligrams per gram of glass.¹

No. of glass.	Kind of glass.	G. iodine solution used.	Mg. As_2O_5 found.	No. of glass.	Kind of glass.	G. iodine solution used.	Mg. As_2O_5 found.
1.....	{ Jena O3832	4.72 5.06	2.1 2.3	9...	{ Jena O1209	10.92 10.74	4.9 4.8
2.....	{ Jena O340	6.23 6.23	2.8 2.8	11...	{ Jena O722	12.34 12.55	5.4 5.6
4.....	{ Jena O144	4.82 4.19	2.1 1.9	13...	{ Jena O578	11.62 11.34	5.1 5.0
5.....	{ Jena O167	5.38 6.02	2.4 2.7	15...	{ Jena O599	5.81 5.93	2.6 2.6
6.....	{ Jena O211	5.78 5.92	2.6 2.6	20...	{ P. P. G. Co. Spectacle Crown	19.94 19.78	9.9 9.8
7.....	{ Jena O2122	10.18 10.19	4.5 4.5	21...	{ P. P. G. Co. Green Plate	3.69 3.51	1.8 1.7
8.....	{ Jena O2071	12.16 12.23	5.4 5.5	22...	{ P. P. G. Co. Dense Flint	18.37 18.25	9.1 9.0

arsenic to the trivalent state during the solution of the glass by sulphuric and hydrofluoric acids, this trivalent arsenic would at the same time be volatilized and therefore the pentavalent arsenic would always be *found* lower than the total arsenic even when the arsenic was entirely in the pentavalent state. The following experiments were tried to test this point.

Known amounts of ferrous sulphate were introduced into the crucible along with measured quantities of arsenic acid and the evaporation with hydrofluoric and sulphuric acids made as before.²

¹ Determinations 1-9 inclusive were made with iodine sol. I; 1 g. sol. equiv. to 0.000446 g. As_2O_5 . Determinations 11-15 inclusive were made with iodine sol. II; 1 g. sol. equiv. to 0.000442 g. As_2O_5 . Determinations 20-22 inclusive were made with iodine sol. III; 1 g. sol. equiv. to 0.000494 g. As_2O_5 .

² Here, as in some previous results, the work was done before the more accurate iodometric method was adopted.

TABLE 6.
Showing both trivalent and pentavalent arsenic in glass, determined iodometrically.¹
Mg. per gram of glass.

Number of Glass.	1	2	4	5	6	7	8	9	11	13	15	P. P. G. Co.		
												20	21	22
Kind of Glass.	JENA.													
	03832	0340	0140	0167	0211	0212	02071	01209	0722	0578	0599	Spec- tacle Crown	Green Plate	Dense Flint
Grams iodine solution equivalent to total arsenic (mean).....	7.13	6.19	6.54	6.86	7.32	11.95	13.26	11.53	14.00	10.42	6.13	21.65	5.61	19.63
Grams iodine solution equivalent to pentavalent arsenic (mean).....	4.89	6.23	4.50	5.70	5.85	10.18	12.20	10.83	12.34	10.27	5.25	19.86	3.60	18.31
Difference.....	2.24	0.04	2.04	1.16	1.47	1.77	1.06	0.70	1.66	0.15	0.88	1.79	2.01	1.32
As ₂ O ₃ in mg., equiv. to difference	0.9	..	0.8	0.4	0.6	0.7	0.4	0.3	0.7	0.1	0.4	0.8	0.9	0.6
Mg. As ₂ O ₃ directly determined (mean).....	2.2	2.8	2.0	2.5	2.6	4.5	5.5	4.9	5.5	5.1	2.6	9.9	1.8	9.1

¹ Determinations 1-9 inclusive given in terms of sol. I; 1 g. sol. equiv. to 0.000446 g. As₂O₃. Determinations 11-22 inclusive given in terms of Sol. III; 1 g. sol. equiv. to 0.000494 g. As₂O₃.

Taken 0.0097 g. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ equiv. to.....	0.0025 g. FeO
Taken.....	0.0116 g. As_2O_5
Found 0.0512 g. $\text{Mg}_2\text{As}_2\text{O}_7$ equiv. to.....	0.0113 g. As_2O_5
<hr/>	
Error.....	0.0003
Taken 0.0193 g. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ equiv. to.....	0.0050 g. FeO
Taken.....	0.0116 g. As_2O_5
Found 0.0153 g. $\text{Mg}_2\text{As}_2\text{O}_7$ equiv. to.....	0.0113 g. As_2O_5
<hr/>	
Error.....	0.0003

Here we took as large a quantity of arsenic as we have found in any glass and much more oxide of iron than would be found in any but very special kinds of glass. It is evident that a quantity equal to 0.5 per cent FeO reckoned on a basis of 1 g. glass has no influence on the determination.

Effect of Ferric Iron on the Separation of Trivalent from Pentavalent Arsenic.—Further thinking on the real nature of the small differences which we call arsenic trioxide led to the suggestion that the true values of arsenic trioxide in the glasses might actually be greater than the values found, because a part of it may have been oxidized to arsenic acid by *ferric* iron in the process of solution of the glass. The following experiment was made to cover this point.

0.050 g. $\text{Fe}_2(\text{SO}_4)_3$ was put into the crucible with 5 cc. 1 : 1 H_2SO_4 and heated a half hour or more on the hot plate to make sure that any nitric acid, which the ferric sulphate sometimes contains, was removed. The crucible was then cooled and 0.0503 g. As_2O_3 was added. The crucible was covered and heated for an hour or more. Then it was cooled again, 5 cc. HF was added and the whole evaporated till white fumes appeared. The residue was tested rigorously with potassium iodide and hydrogen sulphide. No arsenic was found. Therefore all the arsenic was volatilized and none could have been oxidized by the ferric sulphate. Evidently then the presence of ferric iron does not interfere with the separation of the two forms of arsenic by hydrofluoric and sulphuric acids.

Effect of Chlorine in Glass on the Accuracy of the Separation of the Two Forms of Arsenic.—Most, if not all glasses, contain

chlorine, doubtless in the form of chloride. In the Jena glasses analyzed by us, the largest quantity of chlorine found was 0.06 per cent. In an American optical glass 0.16 per cent was found. Glasses made from material less carefully selected may contain still more. According to Dr. E. C. Sullivan, chief chemist of the Corning Glass Works, the largest quantity of chlorine which has been found in any glass in that laboratory is 0.14 per cent. Now since arsenic is volatilized *when either oxide* is heated with hydrochloric acid under favorable conditions, *e. g.*, during the evaporation in the silica determination in a glass, it is quite conceivable that arsenic acid should be reduced by hydrochloric acid and volatilized in the solution of a glass by sulphuric and hydrofluoric acids. (See footnote p. 742.) To test this point, weighed quantities of sodium chloride were heated with given amounts of arsenic acid, sulphuric and hydrofluoric acids. The crucibles contained:

Glass free from arsenic.....	1.00 g.
Arsenic acid solution, 10 cc., equiv. to.....	0.0058 g. As_2O_5
$\text{NaCl} = 0.004$ g. equiv. to.....	0.0025 g. Cl

This was evaporated to dryness in a covered platinum dish. 5 cc. HF was now added and when the salts had dissolved, 5 cc. 1 : 1 H_2SO_4 was also added and the whole evaporated to white fumes. The arsenic was then determined as usual.

11.64 g. iodine solution used in titration; 1 g. solution is equivalent to 0.000494 g. As_2O_5 .

Taken.....	0.00580 g. As_2O_5
Found.....	0.00575 g. As_2O_5
Error.....	0.00005 g. As_2O_5

Again the following quantities of the same substances were used in the same way.

Glass free from arsenic.....	1.00 g.
As_2O_5	0.0029 g.
$\text{NaCl} = 0.0080$ g. equiv. to.....	0.005 g.
$\text{H}_2\text{SO}_4 = 5$ cc.	
HF = 5 cc.	

5.97 g. iodine solution used in titration.

Taken.....	0.00290 g. As_2O_5
Found.....	0.00295 g. As_2O_5
<hr/>	
Error.....	0.00005 g. As_2O_5

These experiments show conclusively that quantities of chlorine of the magnitude found in glasses do not interfere with the separation of the two forms of arsenic.

Influence of Platinum Dissolved from the Crucible on the Separation of the Two Forms of Arsenic.—In the fusion required in the determination of total arsenic a small amount of platinum is dissolved which eventually is precipitated with the arsenic sulphide. This platinum sulphide is somewhat soluble in ammonia and ammonium carbonate. Since platinum is an element of two valencies it is conceivable that reduction by hydriodic acid and subsequent titration with iodine solution might consume a small amount of the latter. Two blanks were therefore made, in which 3 g. Na_2CO_3 and 0.1 g. KNO_3 were fused in a platinum crucible with 0.7 g. and 0.5 g. pure quartz, respectively. Each fusion cake was then treated exactly as in an arsenic determination. A minute black precipitate brought down by hydrogen sulphide was digested with ammonia and ammonium carbonate, oxidized by hydrogen dioxide, reduced and titrated.

No. 1 required 0.16 g. iodine solution, equivalent to 0.08 mg. As_2O_5 .

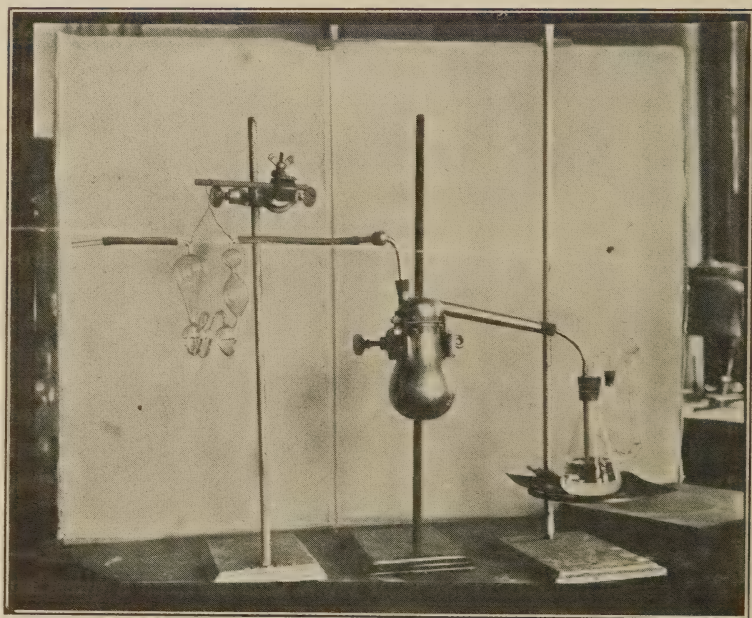
No. 2 required 0.10 g. iodine solution, equivalent to 0.05 mg. As_2O_5 .

Still another blank was made by heating sulphuric acid and hydrofluoric acid in a platinum dish just as in the determination of pentavalent arsenic. The amount of iodine required in titration was 0.18 g., equivalent to 0.09 mg. As_2O_5 . It is therefore obvious that the difference in the results obtained on any glass by the two methods cannot be accounted for by platinum derived from the crucible in fusion, nor can the difference be accounted for by any other influence which may be eliminated by making blanks, for the blanks are of the same order of magnitude.

Separation and Direct Determination of Trivalent Arsenic.—From a purely analytical point of view, it is perhaps a question of no great interest whether the small differences which we found between our series of determinations of total arsenic on the one

hand and pentavalent arsenic on the other really represented the quantity of arsenious oxide present; but in its relation to the chemistry of glass making, this question becomes a matter of more importance.

We were unable to find any considerable error in our results, but as we were still unconvinced of their meaning, we sought positive evidence in the matter by attempting to treat the glasses with hydrofluoric and sulphuric acids in such a way that the volatile material could be caught and examined. In principle, of course, the matter is perfectly simple, but the necessity of using hydrofluoric acid makes a glass apparatus unsuitable since the glass might contain arsenic and the quantity of arsenic in question is very small. Fortunately, we were able to get from the laboratory of the U. S. Geological Survey a small platinum still which could be satisfactorily adapted to the purpose. The head of the still, which is fitted to it by a taper joint, was made tight with



a rubber washer and brass clamps (Fig. 1). The distillate was caught in a caustic soda solution held in a receiver con-

nected to the still by an improvised gold tube and rubber stoppers. The volatile products are swept out of the still into the receiver by a current of air which enters the still through a small platinum tube. The joint between this tube and the head of the still was originally made with a perforated rubber stopper. This worked well when the still was very gently heated, but if the distillation was hurried the results were high, *i. e.*, some pentavalent arsenic was carried over into the receiver. The losses were partly mechanical undoubtedly, and in part due, as we suspected, to the reducing action of the rubber stopper which was at times badly attacked. The latter was, at any rate, eliminated by replacing the rubber stopper by a cork which was protected from the vapors of the still by a thin, close-fitting gold ferrule which made a sufficiently tight joint with the still. The mechanical losses were successfully avoided by dropping into the still, with the reagents and arsenical materials, a few pieces of crumpled platinum foil and 0.5–1.0 g. of lead sulphate. The still was heated by the aid of a radiator.¹

For the most careful tests a gold bottle was substituted for the glass receiver which was always found to be attacked and which might have yielded a little arsenic to the solution.

With these safeguards the direct determination of arsenious arsenic in known mixtures with arsenic acid gave very accurate results. The determination is here a little more complicated than in previous cases because the arsenite solution now contains an excess of fluoride. If this solution were acidified and precipitated hot with hydrogen sulphide, the hydrofluoric acid would attack the glass container and might increase the quantity of arsenic. The alkaline solution was therefore evaporated to near dryness with a little hydrogen peroxide. This of course oxidized the arsenic and permitted the separation of excess hydrofluoric acid by fuming with sulphuric acid. (See p. 751.) The salt cake so obtained was cooled, dissolved in hot water and filtered, after which the arsenic was precipitated with hydrogen sulphide and determined as usual. The results of the separation of small quantities of arsenious acid from arsenic acid are given in Table 7.

¹ See Hillebrand, "Analysis of silicate and carbonate rocks," United States Geol. Survey, *Bull.* 422, 31.

TABLE 7.

Separation by distillation of As_2O_3 from known mixtures with As_2O_5 and determination of the former.

Grams iodine solution required.....	0.16	0.74	1.70	2.32	3.87	4.52
Equivalent to As_2O_3 in mg.....	0.07	0.3	0.7	1.0	1.6	1.9
As_2O_3 taken in mg.....	None	0.3	0.5	1.0	1.5	2.0
As_2O_5 taken in mg.....	116.0	116.0	58.0	11.6	58.0	58.0
Error.....	0.07	0.0	0.2	0.0	0.1	0.1

The necessity of refining the method to this point will be obvious if the reader bears in mind its purpose, which was to decide whether certain small differences between two methods for determining arsenic really and accurately represented arsenious oxide. The method was now applied to a chosen number of the glasses. The results, which are tabulated in Table 8, show

TABLE 8.

Direct determination of trivalent arsenic in glasses compared with the difference between pentavalent and total arsenic.

As_2O_3 in milligrams per gram of glass.

	Jena Optical.							Pittsburgh Spectacle Crown.
	1.	2.	7.	8.	9.	11.	13.	20.
Grams iodine solution required ¹	1.47	0.84	1.37	0.60	0.91	1.28	0.28	2.47
Equivalent to mg. As_2O_3 (A).....	0.6	0.3	0.6	0.3	0.4	0.5	0.1	1.0
Difference between pentavalent and total arsenic mg. As_2O_3 (B)....	0.9	0.0	0.7	0.4	0.3	0.7	0.1	0.9
Difference between A and B in mg.....	0.3	0.3	0.1	0.1	0.1	0.2	0.0	0.1

not only that direct determinations of arsenious oxide in these glasses give positive results, but that these results are of the same order of magnitude as the differences in question. In five out of

¹ 1 g. iodine solution is equivalent to 0.000425 g. As_2O_3 .

eight glasses tested the variation between the direct and indirect determination of arsenious oxide is only 0.1 mg. and in the other three the variation is only 0.3 mg. at the maximum.

It is obvious that the accuracy of the determination might be considerably increased by taking larger portions for analysis, but as our supply of material was limited and the method had been brought to a degree of precision quite sufficient for our purposes, the investigation was pursued no further.

II. Determination of Boric Acid.

The direct determination of boric acid in silicates has hitherto been a tedious process and for this reason this constituent is frequently not reported, or if known to be present is determined by difference. Such a procedure is of course very unsatisfactory since all the errors made in the determination of the other constituents fall upon the boric acid. In order to avoid this difficulty, we directed our efforts toward finding a satisfactory method for the direct determination of boric acid in the Jena optical glasses submitted to us for analysis.

Wherry's Method.—The method originated by Wherry¹ and modified by Sullivan and Taylor² seemed rapid and accurate and probably best adapted to our needs. We made repeated attempts to determine by the modified method the boric acid in a glass containing about 0.5 per cent B_2O_3 , making double precipitations with $CaCO_3$. The results were erratic, and while we have not done enough work on the method to say that some modification of our procedure might not materially improve the results, the necessity of washing out the boric acid in an alkaline solution from bulky gelatinous precipitates is a fundamental objection to it. The tenacity with which such precipitates retain other substances is well known; then, too, we could not avoid the suspicion that with some combinations of elements a substance with the characteristics of boric acid might form insoluble compounds which could not be removed at all. We are aware that the method is used in the laboratories of some of the largest glass works and it is presumably valuable as a control

¹ Wherry and Chapin, *J. Am. Chem. Soc.*, **30**, 1687 (1908).

² Sullivan and Taylor, *J. Ind. Eng. Chem.*, **6**, 897 (1914).

method, but as a method of *high accuracy* it cannot be recommended for *general use*. Wherry himself has expressed the same opinion.

Electrometric Method.—Boric acid can be determined rapidly and accurately by the electrometric¹ method. In order to use this method, in the analysis of glasses, however, the boric acid must first be quantitatively separated from the other constituents in the glass, especially from the arsenic. If the arsenic is present as *arsenic* acid we have an acid whose strength² naturally vitiates the results, and, if present as *arsenious* acid, we have an acid which behaves much like boric acid in the presence of the mannite³ which must be added to the solution when the electrometric method is used.

Chapin's Method.—After the fruitless efforts which we have recounted, Chapin's⁴ method was considered. We may anticipate here by saying that for the determination of boric acid in silicates of such varying composition as the glasses, the method is, certainly at the present time, superior to all others. The description of the method may give one the impression that it is very tedious, but after the apparatus is once set up and the standard solutions are made, the determination can be carried out as rapidly as most of the analytical methods used in the analysis of silicates.

The method of Chapin is a combination distillation and titration method and consists in brief of the following procedure:⁵ The powdered silicate is fused with Na_2CO_3 and the cooled melt taken up with 1 : 1 HCl. The boric acid thus set free is volatilized with pure methyl alcohol as methyl borate in the presence of granular anhydrous CaCl_2 which serves as a dehydrating agent. The distillates are treated with NaOH, either *N*/2 or *N*/5, de-

¹ J. H. Hildebrand, *J. Am. Chem. Soc.*, **35**, 861 (1913).

² Abegg's "Handbuch," Vol. III, part 3, p. 539, and Vol. III, part 1, p. 29.

³ The large amount of alkali used up when As_2O_3 in the presence of mannite is treated with $\text{Ba}(\text{OH})_2$, using phenolphthalein as indicator, proves this.

⁴ *J. Am. Chem. Soc.*, **30**, 1691 (1908).

⁵ The reader is referred to Chapin's description of the method for the necessary details, *J. Am. Chem. Soc.*, **30**, 1687 (1908).

pending on the amount of boric acid present. The NaOH combines with the boric acid and permits the removal of the methyl alcohol by distillation. The alkaline borate is treated with HCl and heated under the proper conditions to expel CO_2 . The solution is now ready for the final titration, which is carried out as follows: The excess of HCl is neutralized with NaOH, using para-nitrophenol to indicate the end point. Mannite is now introduced and the titration of the boric acid carried out using a few drops of phenolphthalein as indicator.

Chapin tried out the method in the presence of such substances as fluorides, and the oxides of arsenic and zinc. These substances are often present as essential constituents of glasses. In every case his results show close agreement between the amount of boric acid taken and found. We have subjected this method to a rather thorough investigation and can in the main confirm his conclusions.

Determination of the Blank.—It was considered advisable to learn if boric acid could be satisfactorily determined under the usual laboratory conditions where one is forced to use glass flasks, such as Jena or Pyrex, which contain boric acid; and also if our chemicals contained boric acid. In the three experiments tabulated below all the flasks used were made of Jena glass. Three grams of Na_2CO_3 were treated with 12 cc. of 1 : 1 HCl in the decomposition flask and one gram of granular anhydrous CaCl_2 per cc. of liquid, added to the solution. The vapors of pure methyl alcohol were passed into the flask until about 200 cc. of the distillate had been obtained. For the final titration we used $\text{Ba}(\text{OH})_2$ ¹ instead of NaOH, since the former can be prepared and maintained free from CO_2 much more readily than the latter. The $\text{Ba}(\text{OH})_2$ was about $N/10$ and was standardized both against HCl and pure fused B_2O_3 , using para-nitrophenol and phenolphthalein as indicators, the titration for the second end point being carried out as usual in the presence of mannite. On account of the volatility of B_2O_3 in a hot solution the titration must be carried out in the cold; therefore if it is necessary to add water to

¹ H. Will, *Arch. Pharm.*, **225**, 1101 (1887); E. Zschimmer, *Chem. Ztg.*, **25**, 442-67 (1901); Sullivan and Taylor, *J. Ind. Eng. Chem.*, **6**, 897 (1914).

the solution for rinsing purposes such water must be free from CO_2 . Undue shaking of the solution must also be avoided on account of the sensitiveness of phenolphthalein to the CO_2 thus introduced. Under these conditions, both end points can be sharply determined. The results of the three experiments mentioned above are shown below:

Expt.	Ba(OH)_2 used. Cc.	Equiv. to B_2O_3 . G.
1.....	0.20	0.0007
2.....	0.25	0.0009
3.....	0.20	0.0007

From these results it is evident that a blank must be made under the same conditions as those which prevail in an actual determination of boric acid. This blank may be due to several causes any one or all of which may be operative: (1) Boric acid may be present in the chemicals, or (2) it may be derived from the glass, (3) finally, the difficulty of getting sharp end points in the solution obtained after the distillation with methyl alcohol may also introduce a plus error. We have noticed repeatedly that the second end point in the final titration is never as sharp as in the titration in the pure aqueous solution used for the standardization of the Ba(OH)_2 . This point will be brought up again later on.

The aqueous solution obtained after removing the methyl alcohol and acidifying were tested for B_2O_3 by the method of Bertrand and Agulhon.¹ We have found this method very satisfactory for small quantities. Boric acid was shown to be present in all our blanks.

Subsequently, we endeavored to determine the source of the B_2O_3 . The glass decomposition flask was replaced by a platinum still, the glass condenser tube with one of silica glass, and the evaporation of the distillate carried out in a platinum vessel. All the other conditions were the same as those in the experiments just described. The titration with Ba(OH)_2 ,² which was

¹ Bertrand and Agulhon, *Compt. Rend.*, **157**, 1433 (1912).

² The Ba(OH)_2 used in these experiments was $\frac{1}{5}$ the strength of the Ba(OH)_2 mentioned in the experiments described above.

carried as usual in the presence of mannite, showed that under these new conditions our blank amounted to 0.7 mg., which is practically identical with results obtained above. We feel confident therefore that no appreciable amount of boric acid was derived from the glass parts of our apparatus.¹ It is probable, however, that this would not have been the case had fluoride been present.

It was also found that a small amount of $\text{Ba}(\text{OH})_2$ was used up in passing from the first end point (para-nitrophenol) to the second (phenolphthalein), when the titration was carried out in distilled water free from CO_2 . The amount of $\text{Ba}(\text{OH})_2$ used was equivalent to 0.3 mg. It is evident therefore that the major portion of the blank is due to the boric acid contained in the chemicals. The amount of the blank obtained in the experiments was constant enough to encourage us to continue our work and determine the correction to be applied to our boric acid values.

In the following experiments known quantities of the boric acid used in the titration of the standard $\text{Ba}(\text{OH})_2$, together with 3 grams of Na_2CO_3 and the other necessary reagents, were used. The boric acid was, as usual, volatilized with pure methyl alcohol.

TABLE 9.

Expt.	B_2O_3 taken. G.	$\text{Ba}(\text{OH})_2$ used. Cc.	B_2O_3 found. G.	Excess. G.
1.....	0.0124	3.85	0.0134	0.0010
2.....	0.0434	12.70	0.0440	0.0006
3.....	0.0764	22.25	0.0772	0.0008
4.....	0.1085	31.56	0.1094	0.0009
5.....	0.1363	36.70	0.1274	0.0011

If the determination has been properly carried out the B_2O_3 found is always greater than that taken. The results also show that the excess is independent of the amount of boric acid taken. We therefore felt justified in applying this excess (average = 0.9 mg.) as a correction to the amount of boric acid found.

¹ Our experience on this point does not confirm Mellor's statement. See J. W. Mellor, "A Treatise on Quantitative Inorganic Analysis" (Griffin & Co., London), p. 586, footnote 2.

In two experiments we found that the amount of boric acid determined was less than the amount taken. This was shown to be due to the fact that the volume of the solution in the decomposition flask was larger than usual and therefore required more CaCl_2 . It is well known that the ordinary anhydrous CaCl_2 has an alkaline reaction. The additional amount of CaCl_2 required in the experiments just mentioned rendered the solution alkaline and prevented the volatilization of part of the boric acid. In carrying out a determination it is well, therefore, to determine the amount of HCl required to neutralize the alkalinity of a unit weight of the CaCl_2 used and add sufficient HCl to the decomposition flask to insure an excess of acid.

This excess, however, should not be unduly large, else too great an amount of NaOH will be required for the neutralization of the acid in the distillate. It has been shown above that our blank was caused almost entirely by B_2O_3 in the reagents, hence the necessity of avoiding an undue excess of any reagent used in the method.

Influence of Impurities in Alcohol.—Chapin has called attention to the fact that commercial wood alcohol will not answer for the determination of boric acid. We have confirmed this and find that the difficulty is caused by a yellow-colored impurity in the distillates which renders an exact determination of the first end point in which para-nitrophenol is used, out of the question. Then, too, the second end point is so indistinct that one can never be sure when it has been reached. In this connection it was thought that possibly another pair of indicators might overcome this difficulty. We did not succeed in finding such a pair, but we did find that when pure methyl alcohol was used, methyl red and thymol blue¹ yielded results which were quite as good as those obtained with para-nitrophenol and phenolphthalein.

One of the more common impurities found in methyl alcohol is acetone. In order to find out if this substance was the cause of the difficulty the following experiments were carried out:

¹ Lubs and Clark, *J. Wash. Acad. Sci.*, **5**, 614 (1915).

Expt.	B ₂ O ₃ taken. G.	Pure acetone in methyl alcohol.	B ₂ O ₃ found. G.	Corrected. G.
1.....	0.0358	1 per cent	0.0364	0.0355
2.....	0.0528	5 per cent	0.0538	0.0529

In (2), the second end point was indistinct and somewhat difficult to determine, which was not the case in (1). The experiments show that while it is not advisable to use an alcohol which contains over 1 per cent of acetone, this impurity is not the cause of the difficulty.¹ Squibb's methyl alcohol (analytical reagent) and Mallinckrodt's pure methyl alcohol gave excellent results.

Influence of Arsenic as As₂O₃.—It is well known that glass usually contains arsenic. In the determination of boric acid in a glass relatively high in arsenic, part of the latter distills over with the methyl borate; it was therefore deemed advisable to investigate the effect of this arsenic on the boric acid determination. Varying amounts of pure As₂O₃,² together with boric acid, were introduced into the decomposition flask along with the necessary reagents. The arsenic carried over into the distillates was determined³ after titrating the B₂O₃.

TABLE 10.

Expt.	B ₂ O ₃ taken. G.	As ₂ O ₃ taken. G.	B ₂ O ₃ found (corrected). G.	As ₂ O ₃ found. G.
1.....	0.0715	0.0110	0.0715	Trace
2.....	0.0702	0.0105	0.0701	0.0011
3.....	0.0743	0.0500	0.0767	0.0245
4.....	0.0795	0.1000	..	0.0568 (a) 0.0110 (b)

In (1), the amount of HCl added was such as to neutralize all bases and leave an excess of about 0.5 cc. conc. HCl. The amount of boric acid found agrees well with that taken, thus showing that

¹ Mellor, *loc. cit.*, p. 586.

² See p. 746 for the method by which the As₂O₃ was prepared.

³ See p. 745 for description of the methods used in making the analyses of arsenic.

the accuracy of the determination has not been influenced by the amount of As_2O_3 taken. In (2), the amount of HCl in excess was about 1 cc. of conc. HCl . The accuracy has not been appreciably affected, though the distillates contain an appreciable amount of As_2O_3 . In (3), the amount of arsenic was increased and the excess of HCl was 2 cc. The end point in this case was very indistinct and the amount of boric acid found was greatly in excess of the amount taken. In (4), 3 cc. of conc. HCl were present in excess of the requirements. The boric acid could not be determined on account of the constant fading out of the second end point. The arsenic was determined separately in the first and second distillates. The amounts are shown in the table and are marked *a* and *b*.

It is evident from these results that if the amount of As_2O_3 present is small and the excess of HCl is only about 1 cc. the determination of boric acid is just as accurate as if no As_2O_3 had been present. The amount of As_2O_3 used in the first two experiments represents the maximum amount ordinarily found in *glasses*. If, however, the substance to be analyzed contains a large amount of As_2O_3 the determination of B_2O_3 becomes inaccurate or impossible unless the As_2O_3 is first oxidized to As_2O_5 in the manner suggested below. The behavior of As_2O_3 under these conditions is not surprising when we stop to consider the ease with which As_2O_3 is volatilized in the presence of HCl .

Influence of Arsenic as As_2O_5 .—It also seemed worth while to know whether *pentavalent* arsenic interferes with the accuracy of the boric acid determination, especially as most of the arsenic in glass is in that form. The As_2O_5 used in these experiments was prepared in the manner described on p. 746.

Expt.	B_2O_3 taken. G.	As_2O_5 taken. G.	B_2O_3 found (corrected). G.	Arsenic as As_2O_3 in the distillate. G.
1.....	0.0762	0.0500	0.0765	0.0018
2.....	0.0745	0.0600	0.0746	0.0019

In both experiments 2 cc. of conc. HCl were present in excess. The results show that the presence of relatively large quantities

of As_2O_5 do not influence the accuracy of the boric acid determination. It is rather interesting to note that some arsenic was carried over into the distillate. This could not have been derived from As_2O_3 which might have been present in the As_2O_5 , because the manner in which the As_2O_5 was prepared precluded the possibility of the presence of As_2O_3 . It is well established that in the presence of concentrated HCl a partial reduction of the As_2O_5 to As_2O_3 takes place.¹ The presence of the trivalent arsenic is thus accounted for. On the basis of these results it appears advisable, where boric acid must be determined in a substance which contains a large quantity of trivalent arsenic, to oxidize the latter in a solution made distinctly alkaline with NaOH before distilling off the boric acid.

Since certain types of glasses contain fluorine, an experiment was carried out in order to learn if this element introduced any disturbing features. A solution containing NaF and B_2O_3 was made alkaline with 20 cc. of $N/2$ NaOH , evaporated to dryness, acidified with HCl and distilled as usual.

B_2O_3 taken.	NaF .	$\text{Ba}(\text{OH})_2$ used. Cc.	B_2O_3 found (corrected).
0.1500	0.200	40.70	0.1517

The determination of the second end point was not as sharp as usual, and the difference between the amount found and taken is greater than the experimental error. Chapin carried out a similar experiment, using, however, a smaller amount of NaF , and obtained very close agreement between the amount of B_2O_3 taken and found. This indicates that the method is very accurate when relatively small amounts of fluorides are present. The method is, however, useful even under the adverse conditions of our experiment.

When small quantities of B_2O_3 , say 2 mg. or less, are to be determined, it will be best to use the method described by Bertrand and Agulhon,² provided all the chemicals are known to be

¹ Abegg's "Handbuch," Vol. III, part 3, p. 539.

² Bertrand and Agulhon, *Compt. Rend.*, **157**, 1433 (1913).

free from B_2O_3 .¹ The method is a very sensitive one and must be carried out with great care.

Finally, we will present a few results showing the close agreement between the determinations when carried out by this method and when the proper correction is applied, on different samples of the same glass. In the table below are tabulated a series of three experiments each on a glass relatively high in B_2O_3 and on one low in B_2O_3 .

TABLE II.

Glass.	Amount of sample. G.	Ba(OH) ₂ used. Cc.	B ₂ O ₃ found. G.	Corrected. G.	% of B ₂ O ₃ .
1.....	{ 0.5000	34.95	0.1311	0.1301	26.02
	{ 0.3000	21.10	0.0792	0.0782	26.06
	{ 0.5000	35.00	0.1313	0.1313	26.06
2.....	{ 1.0000	2.10	0.0073	0.0064	0.64
	{ 1.0000	2.20	0.0076	0.0067	0.67
	{ 1.0000	2.25	0.0078	0.0069	0.69

In the course of our work we have carried out about 50 determinations of boric acid by the Chapin method and have been greatly impressed by its neatness and accuracy.

III. Determination of Some Other Constituents.

A considerable number of the constituents of glass may be satisfactorily determined in exactly the same way as is done in rocks. This is true of silica, chlorine and manganese, also of calcium, magnesium and the alkalis, except when boric acid is present.² In the presence of boric acid only one modification of the usual procedure is necessary. (See p. 779.) But glass contains other elements in addition to those considered in the foregoing pages, the separation and determination of which are rarely called for in rock analysis; or elements which, on account of their quantity or their association with other elements, present

¹ No doubt for very small quantities of B_2O_3 , it will be well to avoid the use of glass apparatus or at least the use of such kinds of glass apparatus as contain B_2O_3 .

² Some glasses contain phosphoric acid; these, of course, demand special methods. We have had no experience with them.

special difficulties to the analyst. We shall make no attempt to cover the whole field—only such portions of it as have come within our own experience, where we have found difficulties and have gained some knowledge of the accuracy of certain methods.

1. Determination of Iron in Optical Glasses.—Since a very little iron colors glass appreciably and lowers its transmission, only a very small amount is permissible in an *optical* glass. The accurate determination of this iron demands several precautions; care must be taken to exclude iron from all outside sources and to avoid loss of iron by occlusion in those precipitations which necessity demand before iron can be determined. First a special sample of about 5 g. of the glass should be prepared by crushing in *agate* instead of steel; a crucible of the purest platinum should be used in the various operations requiring one, especially when the fusions are made. Finally a suitable blank must be made.

Two or three grams of the sample are decomposed with about 3 cc. 1 : 1 sulphuric acid and 5 cc. hydrofluoric acid just as in the determination of pentavalent arsenic. Cool, transfer the residue to a beaker with water and boil till any insoluble sulphate becomes filterable. Filter into a 150 cc. flask, wash, and save the precipitate which may contain as much as 50 per cent of the total iron. Precipitate the filtrate hot with hydrogen sulphide. Thus arsenic and the remaining lead¹ are removed. If zinc is present, proceed according to Waring,² *viz.*, add to the solution before precipitation with hydrogen sulphide a drop or two of methyl orange, neutralize with sodium carbonate and add 0.3 to 0.5 cc. excess of 50 per cent formic acid. In a solution of this acidity zinc sulphide is precipitated in a denser form than in an alkaline solution. Waring draws up the conducting tube above the level of the liquid and corks the flask tight, thus leaving the liquid under a slight pressure of the gas over night. The filtrate from the zinc sulphide which ordinarily contains the major part of the iron is boiled to expel hydrogen sulphide and precipitated by boiling with pure ammonia and a few cc. of hydrogen peroxide.

¹ The amount of lead not precipitated by sulphuric acid is appreciable when the sulphate is filtered immediately after precipitation.

² *J. Am. Chem. Soc.*, **26**, 4 (1904).

If the glass contains lead the insoluble sulphates should first be leached on the filter with a hot concentrated *ammoniacal* solution of ammonium acetate which should previously be filtered if it contains any iron whatever. When the lead sulphate has all been washed through by this means, the residue, whether it contains barium sulphate or not, should be incinerated in the platinum crucible and then fused for a short time with a *weighed portion* of pure potassium or sodium bisulphate. From the cooled mass the iron is extracted by hot dilute sulphuric acid and precipitated like the major portion. Both the very small precipitates of ferric hydroxide are then filtered and washed on the same filter, incinerated in the pure platinum crucible and fused with a *weighed portion* of pure potassium bisulphate for a few minutes at a comparatively low temperature (under a red heat). All the iron is easily dissolved. The remainder of the determination is done according to Hillebrand,¹ *i. e.*, the fused cake is dissolved in water (no sulphuric acid is needed here) and the solution reduced by hydrogen sulphide; the small precipitate of platinum sulphide filtered off, and the hydrogen sulphide expelled from the filtrate by boiling in a current of carbon dioxide which is *washed by a solution of copper sulphate*. This operation is very conveniently carried out in a glass-stoppered wash bottle.

The cold solution is titrated by a very dilute solution of potassium permanganate with the aid of a weight burette. The permanganate is best standardized by sodium oxalate. The blank should be carried out as nearly as may be like the determination itself; especially should the same quantities of hydrofluoric acid and potassium bisulphate be used and the fusions should be conducted in a similar manner as to time and temperature.

Some results are given in Table 12 which may be of interest in showing the minute quantities of iron in optical glasses and the remarkable uniformity of the Jena glasses.

2. The Determination of Zinc.—Zinc may of course be determined in the filtrate from silica, or preferably in the same sample as arsenic and lead.² One or two grams of the glass are

¹ United States Geol. Survey, *Bull.* 422, 107.

² When barium is present the procedure on p. 777 may be followed.

TABLE 12.
Determination of Iron in Some Optical Glasses.

	Jena Optical Glasses.										American Optical Glasses.			
	1.	2.	3.	4.	5.	6.	9.	10.			1.	2.	3.	4.
Weight of glass taken.....	2 g.	2 g.	2 g.	2 g.	3 g.	3 g.	3 g.	3 g.			3 g.	2 g.	2 g.	3 g.
Grams KMnO_4 solution ¹ required..	0.41	0.56	0.60	0.39	0.90	0.62	0.92	0.87			1.49	1.18	0.88	1.27
Grams KMnO_4 solution in blank...	0.16	0.16	0.16	0.16	0.13	0.16	0.13	0.13			0.16	0.16	0.17	0.13
Grams KMnO_4 equivalent to iron..	0.25	0.40	0.44	0.23	0.77	0.46	0.79	0.74			1.33	1.02	0.71	1.14
Grams KMnO_4 solution per g. glass.	0.12	0.20	0.22	0.12	0.26	0.15	0.26	0.25			0.44	0.51	0.35	0.38
Per cent of iron cal. as Fe_2O_3	0.011	0.018	0.020	0.011	0.020	0.013	0.020	0.019			0.040	0.046	0.032	0.029

¹ KMnO_4 Sol. I used for Jena glasses 1, 2, 3, 4 and 6; American glasses 1, 2 and 3; 1 g. sol. equivalent to 0.00091 g. Fe_2O_3 . KMnO_4 Sol. II used for Jena glasses 5, 9 and 10; American glass 4; 1 g. sol. equivalent to 0.00078 g. Fe_2O_3 .

² The results are believed to be accurate within 0.005 per cent.

weighed out, decomposed by hydrofluoric and sulphuric acid and the product evaporated to white fumes. The residue is cooled, transferred to a beaker and diluted. If all is soluble the solution is used directly for the zinc determination. If barium is present the solution should first be boiled for some time to render the sulphate filterable, while if either barium or lead is present the solution should be set aside for the night to insure complete precipitation. The precipitate is then filtered on a Gooch crucible if lead is present, otherwise on paper; the washing in either case following the well known methods. The filtrate and washings¹ are taken for the determination of zinc.

In this solution the arsenic may be precipitated first by hydrogen sulphide or both arsenic and zinc may be precipitated together by the same reagent. In either case before zinc is precipitated, the acidity of the solution should be reduced according to Waring,² and the zinc sulphide brought down in a hot and slightly acid solution. If the sulphides of zinc and arsenic are precipitated together, the precipitate is washed with hot water, the funnel covered with a watch glass and the zinc sulphide dissolved by pouring cautiously under the cover a little hot 1 : 1 hydrochloric acid, while the filtrate is caught in a beaker. After the filter has been thoroughly washed with hot water, it is well to dissolve the arsenic sulphide by pouring a few cc. colorless ammonium sulphide directly on the filter and washing into a separate beaker. A very little zinc sulphide may be left and it is safe, therefore, to treat the filter again with a little hot, dilute, hydrochloric acid, adding the filtrate to the zinc solution. After the hydrogen sulphide has been boiled out of the latter the zinc may be satisfactorily determined by several methods.

Sullivan and Taylor³ add a little more than the required quantity of sulphuric acid, evaporate to dryness, heat to redness and weigh the sulphate. Their results were very good. In some of our determinations we have made a double precipitation of the zinc by sodium carbonate in very slightly alkaline solution, according

¹ Excepting of course the final washing with alcohol when lead is present.

² *Loc. cit.*

³ *J. Ind. Eng. Chem.*, 1, 476, (1909).

to Treadwell,¹ filtering on a Gooch filter and heating inside a large porcelain crucible² to the highest temperature of the Bunsen burner.³

0.1000 g. pure metallic zinc by this method gave 0.1245 g. ZnO equivalent to 0.1007 g. zinc. The following duplicate results on glasses were obtained by separating the zinc in the manner described, precipitating the redissolved sulphide as carbonate and weighing as oxide:

	ZnO found.
Jena optical glass No. 3.....	{ 1.00 per cent 0.96 per cent
Jena optical glass No. 6.....	{ 8.46 per cent 8.61 per cent
Jena optical glass No. 8.....	{ 1.14 per cent 1.24 per cent
Jena optical glass No. 15.....	{ 1.42 per cent 1.46 per cent

A little more accurate but not quite so rapid as the carbonate method is the electrolytic method. If the latter is to be employed, the chloride solution obtained by dissolving the zinc sulphide is first fumed with sulphuric acid in slight excess, cooled and diluted to 100 cc. Pure caustic soda is now added till the precipitated zinc hydroxide is redissolved; then acetic acid in quantity sufficient to precipitate and again dissolve the hydroxide. The solution is acidulated with 0.5 cc. glacial acetic acid, diluted to 150 cc. and electrolyzed at room temperature. To secure good results the following points must be heeded: In the first place zinc cannot be precipitated directly on platinum without alloying with the platinum somewhat and roughening its surface. Also the cathode must be smooth if a uniform, firmly adhering deposit is to be obtained.⁴ To obviate these difficulties the platinum cathode is carefully coated with copper. This may be done by electrolyzing

¹ Treadwell, trans. by Hall, II, 4th ed., Wiley & Sons, N. Y., p. 142.

² *Ibid.*, p. 27.

³ An electric oven of suitable type was not at that time available.

⁴ H. J. S. Sand, *J. Chem. Soc. London, Trans.*, **91**, 383 (1907).

a copper sulphate solution containing 2 per cent nitric acid at a suitable current density. We used a rotating gauze cathode of about 85 cm². available surface, gradually increasing the current from 0.25 to 1.00 amp. over a period of 20 minutes. The cathode was washed with water, then successively by alcohol and ether and dried in a current of air at room temperature. Finally, in the electrolytic precipitation of zinc, a current under 4 volts must be used; otherwise hydrogen will be liberated, the metal will be spongy and will not cling to the electrode. Heeding the above precautions, using the rotating¹ gauze cathode described and electrolyzing with a current which was gradually raised from 0.25 to 2.5 amp. at a maximum of 4 volts, thirty minutes proved sufficient for the deposition of over 0.300 g. of zinc, which adhered well to the cathode. It is unwise to precipitate much more than this amount on a cathode of this area (85 cm².), since larger deposits show a tendency to flake off. The zinc is washed without breaking the current and dried exactly like the copper deposit mentioned above.

A standard sample of zinc from the U. S. Bureau of Standards gave the following results:

	Zinc taken. G.	Found. G.
1.....	0.3227	0.3230
2.....	0.3227	0.3232
3.....	0.2154	0.2159
4.....	0.2154	0.2154

In the first three experiments the zinc was simply dissolved in such an amount of sulphuric acid as to leave about 1 cc. pure H₂SO₄ in excess, after which the procedure was exactly as prescribed above. In the fourth experiment the zinc was precipitated as sulphide, dissolved and further treated like the other three. A comparison of the carbonate and electrolytic methods on a American optical glass follows:

¹ See Gooch and Medway, *Am. J. Sci.*, [4] **15**, 320 (1903); *Ibid.*, **18**, 56 (1904); Exner, *J. Am. Chem. Soc.*, **25**, 896 (1903).

	Carbonate method.	Electrolytic method.
ZnO found.	$\left\{ \begin{array}{l} 1.17 \text{ per cent} \\ 1.12 \text{ per cent} \end{array} \right.$	$\left\{ \begin{array}{l} 1.19 \text{ per cent} \\ 1.20 \text{ per cent} \\ 1.25 \text{ per cent} \end{array} \right.$

Though we have not tried it, the electrometric method for zinc of Bichowsky¹ appears rapid and accurate and would have decided advantages where many determinations were to be made.

3. Determination of Lead and Barium Occurring Together.—

In a glass which contains both lead and barium we have found it best to determine the two together as sulphates; then in a separate portion to determine the barium directly and thus obtain the lead by difference. The lead may also be determined directly but this is more difficult. The details follow:

A weighed portion of glass is decomposed by sulphuric and hydrofluoric acids and evaporated till all the hydrofluoric acid is driven out. The pasty mass after cooling is transferred to a beaker by a jet of water, diluted to about 150 cc., boiled and left to stand over night. The filtering, washing and heating of the precipitate are carried out exactly as with pure lead sulphate.

Barium and lead sulphates cannot be separated by ammonium acetate solution; some of the former is sure to dissolve with the lead sulphate. Barium is therefore determined in a separate portion of glass which is fused with sodium carbonate. The silica is separated as usual, arsenic and lead are precipitated as sulphides by Waring's method,² the alumina, iron, etc., are precipitated by ammonium sulphide, and in the final filtrate from which the hydrogen sulphide has been boiled out the barium is determined as usual. In accurate work it should be noted that the barium sulphate, obtained either by precipitation from dilute solution, or by decomposition of the glass with sulphuric and hydrofluoric acids, always occludes some soluble sulphate and the weight is therefore too high. In two barium glasses which contained less than half a per cent of Na₂O, the barium sulphate

¹ *J. Ind. Eng. Chem.*, **9**, 668 (1917).

² *Loc. cit.*

obtained in the latter way contained the following impurities:¹

0.6293 g. BaSO₄ glass No. 7 contained 0.0052 g. Na₂SO₄.

0.7140 g. BaSO₄ glass No. 8 contained 0.0061 g. Na₂SO₄.

The errors in the percentage of BaO in the above determinations would amount to 0.17 and 0.20 per cent, respectively.

In case a direct determination of lead is desired, the glass should be fused with sodium and potassium carbonates *at the lowest possible temperature* to avoid volatilization of lead oxide. The loss is then very small, if appreciable. The silica is now removed in the usual way except that the operator should wash it more carefully with hot water to remove the lead chloride. In any event it is wise to look for lead in the silica when the latter is volatilized with sulphuric and hydrofluoric acids. The residue should be carefully fused with a very little soda and added to the lead chloride solution. The latter is now made sufficiently acid and precipitated hot with hydrogen sulphide. After standing, the lead sulphide is filtered on a *small* filter, washed thoroughly, and transferred by a jet of water to a small casserole in which it is dissolved in nitric acid and finally evaporated to white fumes with sulphuric acid. The further treatment of the precipitate is carried out as usual, and the little lead sulphide which clings to the filter on which it was washed must be burned at a low temperature in a small tared porcelain capsule and finally fumed with a drop or two of sulphuric acid. The weight of the lead sulphate thus obtained is added to that of the main portion. Sullivan and Taylor² obtain results on lead 0.2 to 0.3 per cent lower when it is determined in the filtrate from silica than when it is determined by decomposing the glass with oxalic and hydrofluoric acids. Our results are similar when sulphuric is substituted for oxalic acid. Thus a glass which gave by the latter method $\left. \begin{array}{l} 35.26 \text{ per cent} \\ 35.26 \text{ per cent} \end{array} \right\} \text{PbO}$, when fused with soda and heated further as described above, gave 35.13 per cent PbO.

A second glass, which by the first method gave 41.64 per cent PbO, gave 41.31 per cent by the second. The lower results

¹ For the method used in this determination see Allen and Johnston, *J. Am. Chem. Soc.*, 32, 588 (1910).

² *Loc. cit.*

obtained by the second method are not necessarily due to the volatilization of lead in the fusion; they are quite as likely due to mechanical losses in the more complicated procedure which this method demands.

4. Separation of Alumina from Barium and Calcium.—Optical glasses not infrequently contain alumina in amounts ranging from 0.5 per cent to 5.0 per cent and sometimes much more. The precipitated alumina accompanied as it is by almost no iron is very difficult to filter,¹ yet when an alkaline earth is present it should be twice precipitated. One of us prefers to precipitate the first time cold with ammonium sulphide, by making the filtrate from zinc and arsenic, which already contains hydrogen sulphide, barely ammoniacal and allowing it to stand over night while the other makes a double precipitation with ammonia. However precipitated, *every filtrate* from the alumina should be evaporated to a small volume on the water bath to make sure no alumina is lost. If any appears it is filtered on a separate filter.

It is possibly not so generally known as it should be that ammonium hydroxide which has stood in glass for any considerable time invariably gives too high results when used to precipitate iron and alumina. Its freedom from silica and alumina or any other impurity which might interfere with the determination should be insured, after which the ammonia should be kept in ceresine or gold bottles.

5. Analysis of Glasses Containing Boric Acid.—Chapters on the analysis of glass including borosilicates, though not found in ordinary text-books on analysis, are given by Classen³ and by

¹ Since iron is determined in a separate sample it would doubtless be better to add to the solution, before the alumina is precipitated, a small, measured volume of a dilute standard ferric chloride solution since, as is well known, an alumina precipitate containing several per cent of iron gives no trouble of this kind.

² The ammonia water used in this laboratory is made as follows. Liquefied ammonia gas is purchased in large steel cylinders from which small distributing cylinders of similar kind are filled. The gas is washed in a little water and absorbed in distilled water contained in a gold bottle packed in ice.

³ "Ausgewählte Methoden der Analytischen Chemie," Braunschweig, 1901, I, 609.

Lunge.¹ The determination of boric acid itself we have already dealt with (p. 761). For the removal of boric acid where it would interfere with the determination of other elements, the same principle is utilized, *i. e.*, volatilization of the boric acid by methyl alcohol partially saturated with hydrochloric acid gas.² To guard against the precipitation of boric acid along with alumina, lime or magnesia, the boric acid should be removed in the progress of the silica determination. When the solution has been evaporated to dryness the *second time* to remove the last of the silica, cool the dish and add 25 cc. or so of the methyl alcohol solution, cover the dish and evaporate again on the steam bath. Repeat the operation, finally rinsing off the cover into the dish. Lunge recommends evaporating 3 or 4 times with methyl alcohol, but so far as our experience goes, two evaporations are sufficient.

Classen and Lunge both determine the alkalies in glass by Berzelius' method, in which the boric acid is volatilized as fluoride along with silica. More satisfactory is the method of J. Lawrence Smith.³ In the decomposition of the glass by this method the boric acid is retained, and must be removed in a subsequent operation. When in the course of this method the chlorides of ammonium and the alkalis have been evaporated to dryness on the steam bath, 10 cc. of the methyl alcohol solution should be added and evaporated with the dish covered. One repetition is all that is necessary, in most cases, for the complete removal of the boric acid. In case of doubt it is a simple matter to repeat the operation on the *weighed* chlorides.

6. Determination of Moisture.—In the complete analysis of a glass it must be remembered that fine mineral powders generally absorb moisture from the atmosphere, the quantity absorbed by any particular mineral depending upon the fineness of the powder, *i. e.*, upon the extent of its surface. It may be surmised that glasses on account of their alkali content would be specially liable to absorb water. On this account the glass should be

¹ "Chemisch-technische Untersuchungsmethoden," Berlin, 1904, I, 666.

² Jannasch and Heidenreich, *Z. anorg. Chem.*, 12, 208.

³ *Am. J. Sci.*, [3] 1, 269 (1871). The method is described also by Hillebrand, *loc. cit.*, p. 171; H. S. Washington, "The Analysis of Silicate Rocks," 3d Ed., Wiley & Sons, N. Y., p. 193 and by Treadwell-Hall, p. 496.

crushed for a moment only, either in a hardened steel or an agate mortar, and then screened, the operation being repeated till sufficient powder is obtained. In this way very fine powder is almost entirely eliminated and only a minimum of moisture is absorbed. Optical glass powders prepared in this way gave the following losses when heated for a few minutes in a covered crucible over a Bunsen burner:

MOISTURE IN GLASS SAMPLES.

No. of glass	Jena Glasses.										American Glasses.			
	1	2	3	4	5	6	12	13	14	15	1	2	3	4
Per cent loss	0.06	0.09	0.20	0.08	0.03	0.14	0.15	0.08	0.08	0.16	0.06	0.10	0.06	..

Two other glass samples, which were inadvertently left in a mechanical grinder for several hours and were consequently very fine, lost on heating 0.68 per cent and 0.88 per cent, respectively.

The following experiments made for another purpose prove that the loss is unquestionably water. A certain glass, which lost 0.10 per cent when heated over a burner, was fused in a Gooch tubulated platinum crucible¹ with dry sodium carbonate, the moisture expelled by dry air and *absorbed by calcium chloride*.

From 1 g. glass was thus obtained 0.9 mg. H_2O = 0.09 per cent.

From 2 g. glass was thus obtained 2.2 mg. H_2O = 0.11 per cent.

7. Gases in Glass.—Low results in the analytical summation of certain glasses led us to consider the question whether gases occur in glass in appreciable quantity. Judging from its composition and the materials used in the manufacture of glass we supposed carbon dioxide was most likely to be found. We selected for the test a glass which from its high content in lime and alkali we believed would have a stronger tendency to retain this gas. 14.73 per cent CaO , 10.37 per cent Na_2O and 0.44 per cent K_2O were found by analysis. For the determination of carbon dioxide we used Borgström's modification² of the ordinary method, in which he decomposes the silicate by a dilute solution of hydro-

¹ *Am. Chem. Jour.*, 2, 247 (1880); Hillebrand, *Bull.*, 422, p. 78.

² *Z. anal. Chem.*, 53, 685 (1914).

chloric and hydrofluoric acids. The gaseous mixture expelled from the decomposition vessel was driven through the usual train of absorbents. Borgström made three blanks in which his soda-lime tube gained from 0.8 to 1.6 mg. This amount he finds is no less when hydrochloric acid alone is used in the decomposition of the mineral.

Since the material which we had to test was *glass*, glass was excluded from certain parts of our apparatus. We used a platinum decomposition vessel and a water-jacketed lead tube as a condenser. Using Borgström's acid mixture in a blank experiment with this apparatus we found a gain of 1.4 mg. in the soda-lime tube. When 3 g. glass was heated in the same way for the same time the gain was 1.7 mg., showing that the carbon dioxide in this glass was small if appreciable. More than that, it is impossible to say on account of the large blank which the method involves.

Far more satisfactory is the following experiment carried out by our colleague Mr. E. S. Shepherd who has had unusual experience in work of this character. Mr. Shepherd very kindly tested the glass in question for gases. A large sample of the glass powder was weighed into a platinum boat which was heated in an evacuated silica glass tube at 1200°. The gases were pumped out and analyzed. Before the gases were measured they were drawn through an absorption tube containing silver oxide¹ and potassium carbonate. 0.0025 g. SO₂ equivalent to 0.87 cc. under standard conditions was removed. This is not included in the analysis.

6.577 g. glass gave 6.55 cc. gas measured under standard conditions. The analysis gave the following volume percentages:

O ₂	= 64.2 per cent
CO ₂	= 24.2 per cent
CO	= 3.5 per cent
H ₂	= 3.9 per cent
N ₂	= 4.1 per cent

99.9

A small fraction of the CO₂, less than 1 cc. at the most, may come from the potassium carbonate through decomposition by

¹ According to Mr. Shepherd, this method of separating SO₂ originated by him is not perfectly sharp but better than any other.

SO₂. Uncorrected the total carbon dioxide amounts to 0.05 weight per cent of the glass, while the total gas amounts to 0.15 weight per cent. If the reader cares to speculate on the source of the different gases it may be stated that the glass contained 0.74 per cent SO₃ which might give rise to the sulphur dioxide and a very little of the oxygen. It contained no arsenic. Whether nitrate was used in the manufacture we do not know. It was not an optical glass. The obvious fact is that glasses may contain an appreciable amount of gas most of which would probably not be included in an ordinary analysis *in any form*.

Composition of the Jena Optical Glasses.—This paper is chiefly concerned with analytical methods, but it will not be out of place to recall the purpose for which the work was originally undertaken, namely, to get information which might be of value in establishing the optical glass industry in this country. The Jena glasses were selected for investigation because of their world-famed excellence; because they are especially well known to scientists through the valuable publications of O. Schott and others; and because a large number of them were immediately available to us.

Table 13 contains nine analyses of Jena optical glasses. Nearly as many more were actually made but those given are typical. About half of them are virtually complete, so far as we know, except for the determination of gases which they probably contain. The summations of the remainder would be raised several tenths of a per cent by the addition of magnesia, sulphur trioxide, chlorine and moisture.

One American optical glass, 3a, is included in the table. It is evidently a copy of No. 5 and is practically as good as its prototype. This glass is also of interest because it contains no arsenic. The most obvious information to be gained from the analyses of the Jena glasses is that they must have been made from very pure raw materials, for the impurities lime, magnesia, sulphur trioxide, chlorine and iron are all present in insignificant quantities. There is practically no iron and extremely little chlorine and sulphur trioxide which in certain glasses are liable to cause milkiness. It is also a safe inference that the pots used must have been not only very low in iron but very refractory,

TABLE 13.
Analyses of Optical Glasses.

Our number	1	3	4	5	3a	8	9	10	11	13 ¹
Schott's number	O3832	O154	O144	O167	—	O2071	O1209	O227	O722	O578
Optical constants { n_D ν	1.5164 64.0	1.5711 43.0	1.5100 64.0	1.6163 36.6	1.6162 36.6	1.6091 58.8	1.6095 56.8	1.5409 59.6	1.5795 53.8	1.5832 46.3
SiO ₂	69.58	54.75	72.15	46.12	46.32	34.56	40.17	59.13	45.02	49.80
B ₂ O ₃	9.91	0.45	5.88	10.96	5.96	3.04	4.50
As ₂ O ₆	0.22	0.14	0.20	0.25	None	0.55	0.49	{	0.55	0.51
As ₂ O ₃	0.09	0.06	0.08	0.04	None	0.04	0.03	0.34	0.06	0.01
SO ₃	0.08	0.12	0.10
Cl.....	0.06	0.06	0.06
Na ₂ O.....	8.44	4.31	5.16	1.72	2.48	0.21	0.13	3.16	0.64	1.24
K ₂ O.....	8.37	7.99	13.85	6.78	5.63	0.09	0.03	9.70	6.80	8.20
MgO.....	0.07	None	0.07	Trace
CaO.....	0.07	0.05	2.04	0.07	0.25	0.03	0.13
BaO.....	2.54	1.64	None	None	46.91	42.35	19.25	22.39	13.36
MnO.....	None	None	None	None	0.004	None	None	None	None
ZnO.....	None	0.96	None	None	1.14	8.17	5.00	15.53	8.03
PbO.....	None	29.30	Trace	45.13	45.03	None	None	None	4.70	18.74
Al ₂ O ₃	0.04	0.04	0.04	0.06	0.02	{	2.79	0.11	{	0.05
Fe ₂ O ₃	0.01	0.02	0.01	0.02	0.03	5.02	0.02	0.02	0.09	0.01
H ₂ O.....	0.06	0.20	0.08	0.03	0.06	0.08
	99.54	99.97	99.74	100.32	99.82	99.48	100.17	99.88	100.28	100.03

¹ For analysis No. 13, the authors are indebted to Dr. E. Posnjak.

for the glasses are almost free from alumina except where it has obviously been added to the batch.

The authors wish to express their thanks for the loan of a number of platinum utensils by the chemical laboratory of the U. S. Geological Survey, which materially facilitated the work.

SUMMARY.

Arsenic.

1. An accurate method for the separation and determination of both trivalent and pentavalent arsenic in glasses is described. (1) The separation depends on the volatilization of the trivalent arsenic as AsF_3 when the glass is heated with hydrofluoric and sulphuric acids, while the pentavalent arsenic remains in the residue. (2) The latter is determined by precipitation as sulphide which is then oxidized to arsenic acid, reduced by hydriodic acid and titrated with a standard iodine solution. (3) The trivalent arsenic is determined by difference between the pentavalent and total arsenic. The determination was controlled by direct determination with the aid of a platinum still. (4) The total arsenic is determined by fusing the glass with sodium and niter, removing the silica and excess nitric acid by evaporation with sulphuric acid and subsequent filtration; and finally proceeding as outlined in (2).

2. These methods for arsenic in glasses are generally applicable to substances in which the arsenic can be transformed into sulphide without loss, and are highly accurate.

3. A comparison of the iodometric method and the magnesium pyroarsenate method for arsenic in glasses is made. The former has the advantage in accuracy, and also in speed except where occasional determinations are called for.

Boric Acid.

1. For the determination of boric acid we have found that Chapin's method is very reliable and yields highly accurate results.

2. It has been shown that in order to obtain very accurate results, a "blank" must be made and the value applied as a correction to the amount of boric acid found. The correction is small and for ordinary work can be neglected.

3. The accuracy of the method is very appreciably affected by relatively large amounts of *arsenious* acid but not by *arsenic* acid. Boric acid can therefore be satisfactorily determined in the presence of large amounts of arsenious acid by oxidizing the solution with H_2O_2 after making it distinctly alkaline with NaOH.

4. Relatively large amounts of fluorides appreciably affect the accuracy of the determination but do not seriously impair its usefulness for ordinary work.

Other Determinations.—Our experience with the following cases in glass analysis is detailed: (1) the determination of the minute quantities of iron in *optical* glass; (2) the separation and determination of zinc; (3) the separation and determination of lead and barium occurring together; (4) the separation of calcium or barium from relatively large quantities of aluminum occurring with almost no iron; (5) the determination of those elements in boric acid glasses with which the boric acid interferes.

Attention is called to the universal presence of hygroscopic moisture in powdered glass samples.

Some data by Mr. E. S. Shepherd on gases in glass are given.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTION OF WASHINGTON,
WASHINGTON, D. C., January 15, 1919.

THE CONDITION OF ARSENIC IN GLASS AND ITS ROLE IN GLASS-MAKING.

By E. T. ALLEN AND E. G. ZIES.

The condition of arsenic in glass has been a mooted question with glass-makers. O. Schott¹ of the Jena glass works regarded all the arsenic in *optical* glass as present in the form of arsenate which, he believes, is a product of the reaction between the arsenious oxide and the alkali nitrate of the batch. Where nitrate is not added to the batch it is Schott's opinion that the arsenic is entirely volatilized from the molten glass; in other words that glass never contains arsenic in the form of the lower oxide. On the other hand, W. Rosenhain¹ of the Chance Glass Works reasoned from the general chemical behavior of arsenic that glass must contain only the trivalent form.

F. Gelstharp² found experimentally that when arsenious oxide was fused with sodium carbonate in an open crucible at 940° , a part of it was volatilized, and, of the remainder, the major part was oxidized to arsenate. When arsenious oxide was heated with calcium carbonate to 1090° , again a portion of the arsenic was lost, while the rest was all oxidized to arsenate. Thus it appears that the air alone is capable of oxidizing arsenious oxide when thus heated with lime or soda. Gelstharp found that even sodium sulphate oxidized arsenious oxide when fused with it in a covered crucible, as was shown by the formation of sodium sulphide. He further states that the Pittsburgh plate glass was found by him to retain 56 per cent of the arsenic put in, entirely in the form of arsenate.

Our own results show that in all the glasses tested, both plate and optical glasses, the major part of the arsenic present exists in the pentavalent state but that nevertheless a portion exists in the trivalent state.³

¹ Hovestadt, "Jena Glass, etc." Translation by J. D. and A. Everett. Macmillan and Co., New York, 1902, p. 412.

² *Trans. Am. Ceram. Soc.*, 15, 585 (1913).

³ See the preceding paper in THIS JOURNAL.

Role of Arsenic in Glass-Making.—Arsenious oxide is used in glass-making with two distinct purposes. In some cases it is supposed to "whiten" the glass. With this function we are not concerned in this paper.

Arsenious oxide is also used in fining or removing the small bubbles from glass; it causes the glass to "boil," in which operation the small bubbles are apparently swept out by larger ones. Other substances which give off gas at high temperatures are used at times for the same purpose—wood, potatoes, etc. Just what the chemical behavior of arsenic in the fining process may be is little understood. Schott¹ suggests that it may depend on the dissociation of arsenates at high temperature attended by the liberation of oxygen. As Schott has elsewhere expressed the view that glass cannot retain arsenic in the trivalent condition, this dissociation should result in the liberation and loss of arsenious oxide as well as oxygen.

Very accurate methods for the determination of both oxides of arsenic now enable us, with the aid of information from the manufacturers, to compare the condition and quantity of arsenic in the finished glass with that of the batch. In the table is given the history of the arsenic in three American optical glasses made at the factory of the Spencer Lens Company at Hamburg, N. Y. The mixing of the batches was very carefully superintended by Dr. C. N. Fenner of the Geophysical Laboratory, from whom we obtained the samples and the composition of the batches from which the percentages of arsenic in the finished glass could be calculated. The history of each pot is known in detail. The table also contains data on two plate glasses. From the batch of each, both plate and optical glasses, we have calculated the percentage of arsenic (as trioxide) which would be found in the finished glass, on the assumption that no arsenic, boric oxide, or alkali was volatilized in the furnace; in other words, that only moisture, carbon dioxide, and oxygen (from KNO_3) were lost. Losses of boric oxide and alkali would of course raise these figures a trifle, but probably not by an appreciable amount. The percentages are given in the table. The table further contains the quantities

¹ Doelter, "Handbuch der Mineralchemie," Leipzig, I, 861 (1912).

of trivalent and pentavalent arsenic which we have found in each of the glasses by methods detailed in the preceding article in *THIS JOURNAL*. From these figures the loss of arsenic was readily calculated. All the glasses have certainly lost arsenic, though of course it is impossible to say *at what stage* of the process it was lost. The green plate was the only glass of the batch to which niter was not added, and here the loss of arsenic is distinctly larger. With this exception the losses are of a similar order of magnitude. Concerning this loss of arsenic, an observation made by R. L. Frink¹ is of considerable interest. He found, in the bubbles or "seeds" of a glass, crystals which were identified both microscopically and chemically as arsenious oxide. So far as it goes, this observation supports the hypothesis of the dissociation of arsenic pentoxide and the volatilization of arsenic trioxide. Thus it appears that arsenic trioxide is oxidized at low

TABLE.

Showing the condition of arsenic in the finished product and the loss of arsenic in the making of five American glasses.

Kind of glass.	Taken. As ₂ O ₃ . %.	Found.			Lost in % of glass.	Lost in % of As ₂ O ₃ .
		As ₂ O ₃ . %.	As ₂ O ₃ . %.	Total arsenic cal. as As ₂ O ₃ . %.		
1. { "T" Medium flint containing 42 per cent PbO	0.48	0.38	0.05	0.38	0.10	21
"P" Light flint containing 38 per cent PbO....	0.40	0.35	0.05	0.35	0.05	12
"V" Baryta flint containing 38 per cent PbO and 6 per cent BaO	0.26	0.23	0.03	0.23	0.03	11
2. { Spectacle crown	1.09	0.99	0.08	0.93	0.16	15
Green plate.....	0.36	0.18	0.09	0.24	0.12	33

1. Optical glasses manufactured by the Spencer Lens Co. at Hamburg, N. Y.

2. Optical glasses manufactured by the Pittsburgh Plate Glass Co.

¹ *Trans. Am. Ceram. Soc.*, **17**, 798 (1915).

temperature and the product formed is stable enough to remain until a high temperature is reached and the glass becomes fluid, when it slowly dissociates into oxygen and arsenic trioxide, both of which aid in the fining.

Further consideration of this interesting question must be postponed until we have more data on the behavior of arsenates and arsenites at high temperatures.

The authors wish to express their thanks to the authorities of the Pittsburgh Plate Glass Company and the Spencer Lens Company, and also to Dr. Fenner for the information and material which they very kindly placed at our disposal.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTE OF WASHINGTON,
WASHINGTON, D. C., January 15, 1919.

THE PARTIAL PURIFICATION OF ZIRCONIUM OXIDE.

By A. J. PHILLIPS, Emporium, Pa.

Zirconium oxide is a very desirable refractory for use at high temperatures, its high melting point as well as its low coefficient of expansion causing it to be very satisfactory with respect to checking and spalling upon rapid heating and cooling; likewise its low thermal conductivity renders it very desirable as an insulating material in certain kinds of work.

In the course of some work on spark plug bodies a considerable quantity of the oxide was required for experimental purposes, the specification calling for less than 0.1 per cent of Fe_2O_3 . A search was therefore made for a method which would remove the iron oxide alone, the material thus purified and still containing silica, alumina and oxide of titanium being sufficiently pure for the purpose.

The crude zirconia secured from the Foote Mineral Co. of Philadelphia was received already ground to a fineness of 75 per cent through the 100-mesh sieve and recourse was made to the effect of sintering it with various fluxing agents. Sintering with sodium carbonate gave an incompletely decomposed product which on leaching with weak acid filtered very slowly and still contained too much iron oxide to be satisfactory; furthermore the amount of manipulation involved was excessive.

Roasting with ammonium chloride removed very little of the iron as chloride and roasting with sodium chloride to 1500°C gave a product containing considerable amounts of fixed alkali and an iron oxide content of 1.5 per cent. Repeated treatments with sodium chloride did not lower the iron oxide content, while the alkali content increased with each treatment.

A search of the literature showed a large number of methods reported for the decomposition of zircon, a rather complete bibliography being given by J. W. Mellor.¹

In order to compare several of these methods of decomposition

¹ "Quantitative Inorganic Analysis," Vol. 1, p. 499.

a sample, usually 10 grams, was incorporated with a "decomposer," molded into a small cylinder and fired in a direct flame to 1200–1300° C. After the firing the ignited material was ground, treated with a 10 per cent solution of hydrochloric acid for two hours and filtered. A weighed portion of the residue was then fused with sodium bisulfate and the iron after reduction with hydrogen sulfide, titrated with permanganate. In the following table is given the percentage of iron oxide remaining after several different methods of treatment.

TABLE I.

Composition.	Per cent Fe_2O_3 .
1..... 1 part ZrO_2 + 1 part Na_2SO_4 + $\frac{1}{3}$ part C...	1.70
2..... 1 part ZrO_2 + 1 part Na_2SO_4 + 1 part C....	1.79
3..... 1 part ZrO_2 + excess of Na_2S	0.88
4..... 1 part ZrO_2 + 1 part NaCl	1.68
5..... 1 part ZrO_2 + 1 part NaCl + $\frac{1}{2}$ part C....	1.45
6..... 1 part ZrO_2 + 1 part NaFl	0.92
7..... 1 part ZrO_2 + 1 part NaFl + $\frac{1}{2}$ part C....	0.79
8..... 1 part ZrO_2 + $\frac{3}{4}$ part NaFl + $\frac{1}{4}$ part Na_2SO_4	0.91

The use of sodium sulfide as a flux was not as satisfactory as the results appear, since further treatment did not seem to have any effect on the remaining iron oxide. Further work was then done with the fluorides as they had the best effect, although two well-known methods of fluoride decomposition were not tried; one using a mixture of sodium hydrate and sodium fluoride, the other acid potassium fluoride, as both methods would involve the use of containers on account of the fluxing of the mixture.

A consideration limiting the use of various reagents was found in the amount of zirconia rendered soluble by leaching with hydrochloric acid in each case. In all of the treatments the leachings were reduced with hydrogen sulfide and boiled with a solution of sodium thiosulfate, in order to precipitate the hydroxides of zirconium, titanium and aluminium. It was necessary to reduce first with hydrogen sulfide, since before the liberated sulfur dioxide reduced the iron to the ferrous condition, the precipitate formed absorbed or occluded ferric iron which was not subsequently reduced and removed by the sulfur dioxide—even after the reduction the precipitated material was not entirely free from iron

oxide. It was therefore thought important to weigh the residues in each case after the acid treatment and ignition, in order to determine how much was rendered soluble and would require further treatment.

TABLE 2.

Composition.		Per cent residue.	Per cent Fe ₂ O ₃ .
1.....	1 part ZrO ₂ + 1/2 part KBF ₄	58.29	0.70
2.....	1 part ZrO ₂ + 1/2 part (1/2 NaFl + 1/2 Na ₂ S ₂ O ₇)..	73.53	0.85
3.....	1 part ZrO ₂ + 1/2 part (3/4 NaFl + 1/4 C).....	66.62	0.79
4.....	1 part ZrO ₂ + 1/2 part (3/4 Na ₂ S ₂ O ₇ + 1/4 C).....	81.00	0.96
5.....	1 part ZrO ₂ + 1/2 pt. (2.5 pts. CaFl ₂ + 1 pt. H ₃ BO ₃)	64.40	1.21
6.....	1 part ZrO ₂ + 1/2 part (5 CaFl ₂ + 1 Na ₂ B ₄ O ₇)....	52.62	1.15
7.....	1 part ZrO ₂ + 1/2 part (5 NaFl + 1 Na ₂ B ₄ O ₇).....	63.40	0.62
8.....	1 part ZrO ₂ + 1/2 part (1/2 Na ₂ S ₂ O ₇ + 1/2 Na ₂ B ₄ O ₇)	61.20	0.69

Table 2 shows the composition of the material ignited; the percentage of material remaining after igniting, leaching with acid and again igniting; and the percentage of iron oxide remaining after the treatment.

The first mixture fused and it was necessary to run it over in platinum; the others were brittle and pulverized readily. All of the mixtures containing sodium pyrosulfate filtered poorly—due to the presence of much gelatinous material. In general the sodium fluoride-borax mixture was the best, but even its behavior was not entirely satisfactory as evidenced by the presence of 0.62 per cent residual iron oxide. In cases where calcined zirconia is ground and dissolved in hydrofluoric acid in order to effect subsequent precipitation as potassium zirconium fluoride, the use of this mixture would be advantageous since no container is required for the fusion, whereas, when an acid fluoride is used, a graphite or carborundum crucible is necessary.

The possibilities of acid treatment alone were then considered, since Wedekind¹ has recommended continued digestion with this acid and Rosenhain² states that the impure material readily stands a temperature of 1600° C while the refractory qualities are much improved by digestion with hydrochloric acid to remove a part of the iron oxide.

¹ *Berichte*, 43, 290-7 (1910).

² *Met. Chem. Eng.*, 15, 674 (1916).

For the acid tests, 10 grams of powder, which passed the 100-mesh sieve, were digested with 50 cc. of acid for three hours on a steam plate at 100°C and the iron oxide in the residue determined. In addition the effect of a small amount of pressure or at least the prevention of the volatilization of the acid was effected by placing the powder and acid in a small bottle with a spring cover and heating it in boiling water. In two cases the acid was first saturated with chlorine gas. The results were as follows:

Compositions.		Per cent Fe_2O_3 in residue.
1	10 grams powder, 50 cc. HCl	1.52
2	10 grams powder, 50 cc. HCl in bottle	1.40
3	10 grams powder, 50 cc. HCl sat. with Cl	1.48
4	10 grams powder, 50 cc. HCl in bottle sat. with Cl	1.34

A few other tests were made involving the use of HCl; in one of them the zirconia was acid-treated after having been heated to 900°C for three hours in a current of hydrogen. The results were not satisfactory. In another case dry hydrochloric acid gas was used instead of hydrogen and while the iron oxide not removed by digestion with acid was reduced to 0.62 per cent, yet this was considered still too high.

Chlorine gas was then tried on a small scale by passing it over the ore in an electrically heated tube. The results were so encouraging that a gas-heated furnace was built in which the ore was heated in an upright cylindrical muffle, while chlorine was introduced at the bottom through a piece of glazed pyrometer tubing.

The simultaneous use of chlorine and carbon as explained by Thomsen¹ causes a great reduction of the temperature at which the iron oxide is decomposed. In the succeeding work, therefore, the crude zirconia was mixed with about 4 per cent of finely powdered petroleum coke, molded into small balls and heated in the muffle in an atmosphere of chlorine to 900°C .

The question of retorts in which to conduct the chlorination is an important one and probably a dense, completely vitrified material resembling chemical stoneware would be most satisfactory. The cylinders first used were jiggered from a mixture

¹ "Thermochemistry," p. 357.

of 55 per cent grog passing an 8-mesh but retained on a 30-mesh sieve, 35 per cent Florida kaolin and 10 per cent Tennessee ball clay. While withstanding the rapid heating and cooling employed, they were entirely too porous, the chlorine penetrating and coming through the walls as shown by their whitening. A better mixture was later secured, it being a glass-pot mixture of Laclede Christy bond clay, Illinois and Newark kaolins, Arkansas and Highlands fireclays with 60 per cent of 12-mesh grog composed of North Carolina kaolin and calcined Highlands fireclay. This cylinder became red with repeated use, showing the penetration of iron oxide, and apparently grew denser with time. Porcelain jars were tried but cracked with rapid temperature changes and porcelain inlet tubes for the chlorine became very porous even though not heated to any extent.

To further increase the density of the cylinders they were painted with a mixture of sodium silicate and clay which on heating fused to a smooth glaze. On the external surface the glaze coating was slowly volatilized, but on the inner surface a dense, white salt coating was formed which did not spall to any appreciable extent.

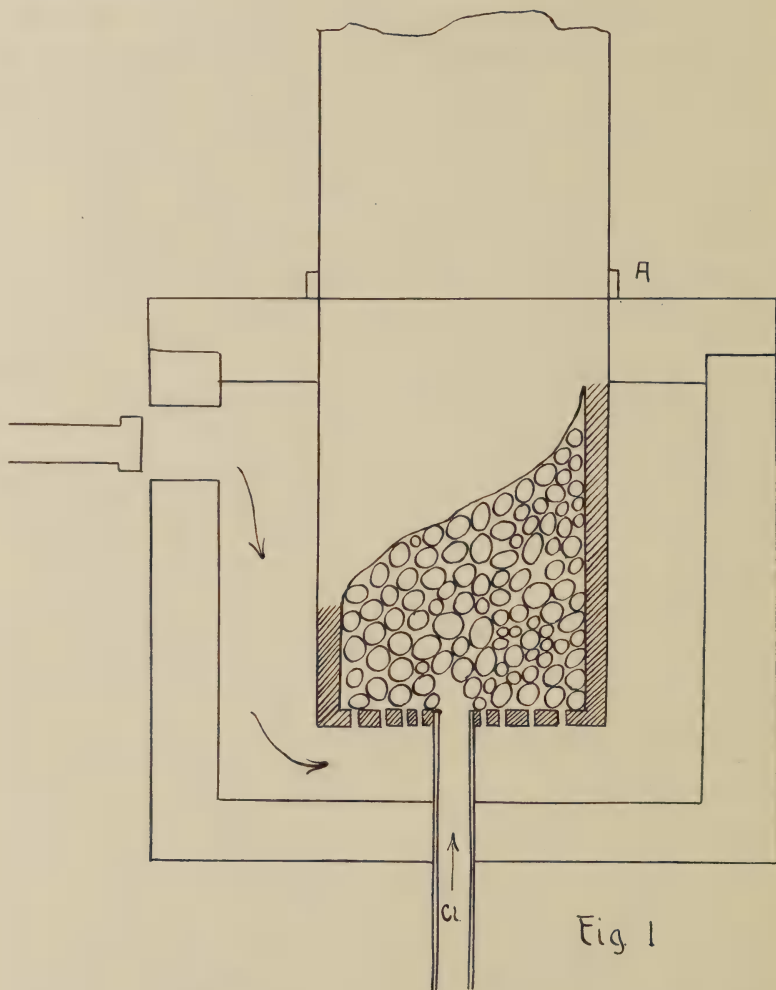
It was soon found that zirconium chloride was being volatilized out of the furnace along with the iron chloride, for on dissolving some of the sublimate in dilute HCl, neutralizing, saturating with SO₂ and boiling the solution, a considerable precipitate of hydrated zirconia was secured.

Prescott and Johnson,¹ state that zirconia with charcoal is volatilized as the chloride in a current of chlorine.

In order to recover this material a cylindrical reverberatory type of furnace was built with a long cooling chamber. It was also thought that passing the products of combustion over the material would maintain a reducing atmosphere which might result in cutting down the amount of carbon required in the raw mix. However, the fact that the chlorine sank to the bottom of the cylinder and was swept out by the current of gases kept the balls at the top from being properly chlorinated unless a large excess was used; therefore a return was made to vertical chlorination, an up-draft furnace being used and the products of com-

¹ "Qualitative Chemical Analysis," p. 203.

bustion passed through the mix. The construction of the furnace is shown in Fig. 1.



With this furnace the top was closed and the gas and air introduced near the top, the draft being upward through holes in the bottom of the cylinder. Owing to the limited space, combustion was very imperfect and it was necessary to keep the tip of the

burner partly outside of the furnace. The result of this partial combustion was that a considerable quantity of water vapor was formed and condensed at the joint A, so that the clay luting around the joint was dripping wet during over half the run, and water vapor with HCl gas issued from the stack throughout the run. The effluent contained considerable iron oxide as shown by its red color as it dried on the outside; however, an examination of the material showed that little or no zirconia was present and it was suggested that external heating be used and that the chlorine be passed through water. This was finally the method adopted, the chlorine being passed through a bubble tube near the furnace. Cold water was not nearly so efficient as hot water in the bubble tube in retarding the choking of the apparatus with volatilized iron chloride and probably for larger installations the injection of low pressure steam along with the chlorine would be most satisfactory.

In chlorinating with external heating and exposure of the material to the air at the top of the furnace, peculiar incrustations like "Pharaoh's serpents" collected over the top layer, whereas, in cases where up-draft and a stack were used, the sublimate was deposited as a fine powder upon the walls—the color in most cases being an indication of how much zirconia had been volatilized along with the iron oxide.

An interesting fact was that apparently the size of the specimens made no difference, as balls from $\frac{1}{4}$ in. to 1 in. diam. were chlorinated at the same rate and the necessity for the fine grinding usually specified in decomposing this material was entirely obviated—the raw material with only 75 per cent passing the 100-mesh sieve being successively used.

The penetration of the chlorine was shown by the fact that in every case where a ball was white on the outside, it would also be white on the inside right to the core. In a few cases some of the balls at the top of the cylinder were white on the inside and yellow or coated with yellow crystals on the outside. This was evidently caused by iron chloride being volatilized lower down in the hotter part of the furnace and being deposited on the cooler material near the top.

The question then arose as to whether or not it would be possible to chlorinate the material without first mixing with a binder and molding into balls. Very probably, however, this would be possible only if a rotating drum were used since there is always some iron chloride which collects at the top layer of material and which would sooner or later choke the furnace and shut off the flow of chlorine.

It would be possible then to press the crude zirconia into bricks with a little binder, pile them in checker work in a furnace and chlorinate them in place—if it were not for the fact that chlorination removes the iron oxide bond in the material and after chlorination it is very mealy, porous or punky. The oxide being heavy, the bricks would then fall to pieces or at least crush those at the bottom of the pile. Even by firing to cone 35, which was done in some cases in calcining the finished material, a very slight bond was developed, the specimens being porous and not permitting much handling.

In order to secure more quantitative figures as to the loss of zirconia, two samples were chlorinated in an electrical tube-furnace under the same conditions except that in one case the chlorine was passed through cold and in the other, boiling water. The analyses as given below show (1) for cold and (2) for boiling water.

	1. Per cent.	2. Per cent.
SiO ₂	15.52	11.49
Al ₂ O ₃	2.44	1.87
Fe ₂ O ₃	0.04	0.03
CaO.....	0.68	0.49
P ₂ O ₅	0.05	0.03
Na ₂ O.....	0.06	0.05
K ₂ O.....	0.09	0.08
ZrO ₂	80.91	85.93
TiO ₂	0.18	0.16

If we take the following analysis (3) of the raw material and calculate out the ignition loss and the oxides removed by wet chlorine, *viz.*, Fe₂O₃, MnO₂, P₂O₅, and TiO₂, we obtain a theoretical composition as shown in (4):

	3. Per cent.	4. Per cent.
SiO ₂	10.62	11.56
Al ₂ O ₃	1.71	1.86
Fe ₂ O ₃	2.90	...
CaO.....	0.42	0.45
P ₂ O ₅	0.65	...
Na ₂ O.....	0.04	0.04
K ₂ O.....	0.06	0.06
ZrO ₂	79.25	86.31
TiO ₂	1.81	...
Ig Loss.....	2.78	...

By comparing analysis 4 with 1, about 5 per cent, and with 2, less than 0.5 per cent ZrO₂ was lost in chlorination.

In explaining the course of the reactions, we might suppose that the chlorides of iron and zirconium would be formed and volatilized at the same rate with a loss of zirconium chloride at least equal to that of the iron chloride. However, Mellor¹ states that if a certain resistance is to be overcome before a reaction can be started, the process which requires the least energy for its initiation will be produced in preference; furthermore, if the two reactions have actually started side by side, the relative velocities of the two reactions will determine which one takes place to the greatest extent. Iron chloride volatilizes at 100° C while the zirconium chloride volatilizes at or about 400° C; so it is probable that there is a preferential formation and volatilization of the iron chloride. As the temperature is gradually raised we have the establishment of a reversible reaction, $\text{FeCl}_3 \rightleftharpoons \text{FeCl}_2 + \text{Cl}$, or, according to Burgess,² two independent components form the system which is divided into three phases, FeCl₃, FeCl₂ and Cl. The system is therefore mono-variant and admits a curve of dissociation temperatures. Therefore at any temperature T, equilibrium corresponds to a tension P of the chlorine atmosphere which is determined by a knowledge of the temperature T. If the rate of chlorine introduction is increased so that the pressure becomes greater than P, the FeCl₂ again absorbs Cl until the pressure equals P and if the chlorine is reduced, FeCl₂ is reduced

¹ "Chemical Statics and Dynamics," p. 325-6.

² "Thermodynamics and Chemistry," p. 155.

until the pressure takes its former value. In other words, an equilibrium is constantly tending to be formed.

Now with the introduction of water vapor the equilibrium is disturbed; there is a partial decomposition of the vapor into hydrogen and oxygen which reacting with the chloride tends to the formation of a new equilibrium containing among some other products, oxide of iron and hydrochloric acid gas. If we apply the same considerations to the zirconium chloride we shall establish a system containing some zirconia and hydrochloric acid gas. There would thus be no advantage in the introduction of water vapor if it were not for the fact that iron oxide mixed with carbon is volatilized as the chloride in a current of hydrochloric acid gas while zirconia is not affected thus; so that as we have an excess of carbon present the conditions are favorable for the removal of the iron oxide alone.

Thus as the action to a large extent depends on hydrochloric acid gas, it might seem advantageous to use it throughout in decomposing the material, but in the tests made the decomposing action of the hydrochloric acid gas was not sufficient to remove the last 0.5 per cent of iron oxide, the more energetic chlorine being required to break up the combination in which the iron oxide exists in the crude zirconia.

It is obvious that the treatment is applicable not only to the purification of crude zirconia, but also to bauxite and flint for the removal of iron oxide.

In conclusion we beg to acknowledge our indebtedness to Mr. A. V. Bleining of the Bureau of Standards, for suggestions and assistance in outlining the work.

STRENGTH TESTS OF PLAIN AND PROTECTIVE SHEET GLASS.¹

By T. L. SOREY, Washington, D. C.

This paper deals with strength tests of plain sheet glass and one type and make of protective glass. The protective glass, which will be designated as Type A, consists of sheet glass to one side of which is firmly attached a thin sheet of celluloid. The intention is that the glass shall be used with the celluloid or treated side toward the person to be protected. This is one of several kinds of protective glass which are to be investigated and therefore at present no statement can be made as to the value of this glass compared with other protective types. However, the effect of the thin coating of celluloid on the mechanical properties of the glass is interesting, and the presence of this coating enables us to study the manner in which sheet glass is fractured by various forces.

The samples were subjected to firing tests, impact tests and cross bend tests as follows:

Firing Tests.

The sheets of glass used for this test were 8" by 10" and of three thicknesses, $\frac{1}{8}$ ", $\frac{3}{16}$ ", and $\frac{1}{4}$ ". The $\frac{1}{8}$ " and $\frac{1}{4}$ " thicknesses were plate glass while the $\frac{3}{16}$ " thickness was tested in both a plate and a special blown window glass. One lot of glass of each thickness was plain and another was Type A protective glass.

The samples were clamped firmly to a board frame with bearings on rubber strips $\frac{3}{16}$ " thick. One set of bearing strips was near the edges of the glass and another around a rectangular hole, $2\frac{1}{2}$ " by 5", at the center of the sheet. The samples were then perforated by bullets fired from a regulation army rifle at a distance of fifty feet.

The following observations were made from the results of the firing tests:

¹ By permission of the Director, Bureau of Standards.

A. Plain glass:

All samples were completely broken and shattered.

B. Type A protective glass:

1. The glass remained in place with the exception of a small area, in the immediate vicinity of the point of entrance, which was pulverized and carried through with the bullet.

2. The thinner the sheet the fewer the cracks.

3. A smaller hole and fewer cracks resulted when the bullet entered perpendicularly to the surface than when it entered at an angle of 45° .

4. Fewer cracks resulted when the bullet entered from the treated side.

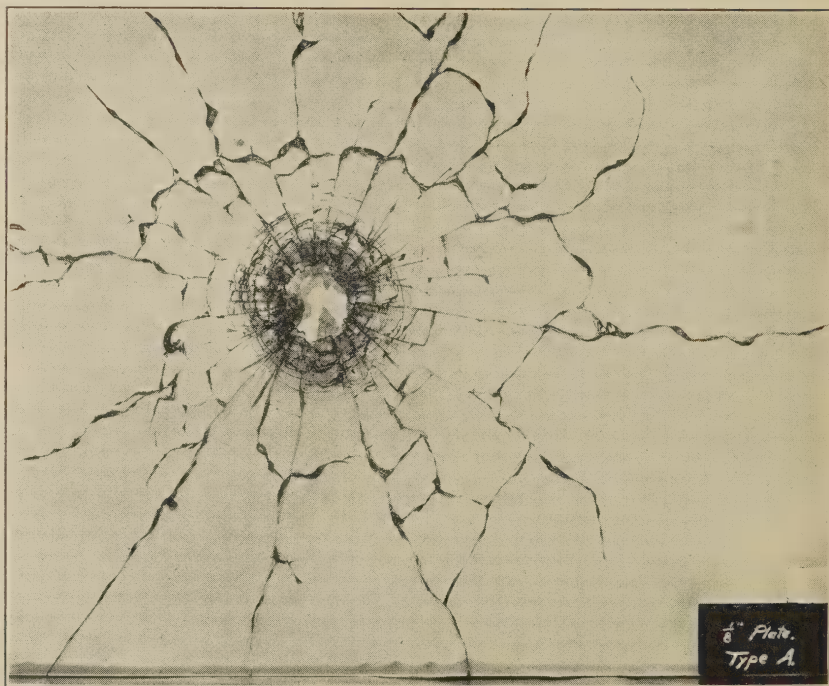


FIG. 1.

5. The effect of the shock was less on blown window glass than on plate glass of the same thickness.

6. When the cracking was the most extended as in a few of the thickest samples, the plate bent at the middle but was held together by the celluloid.

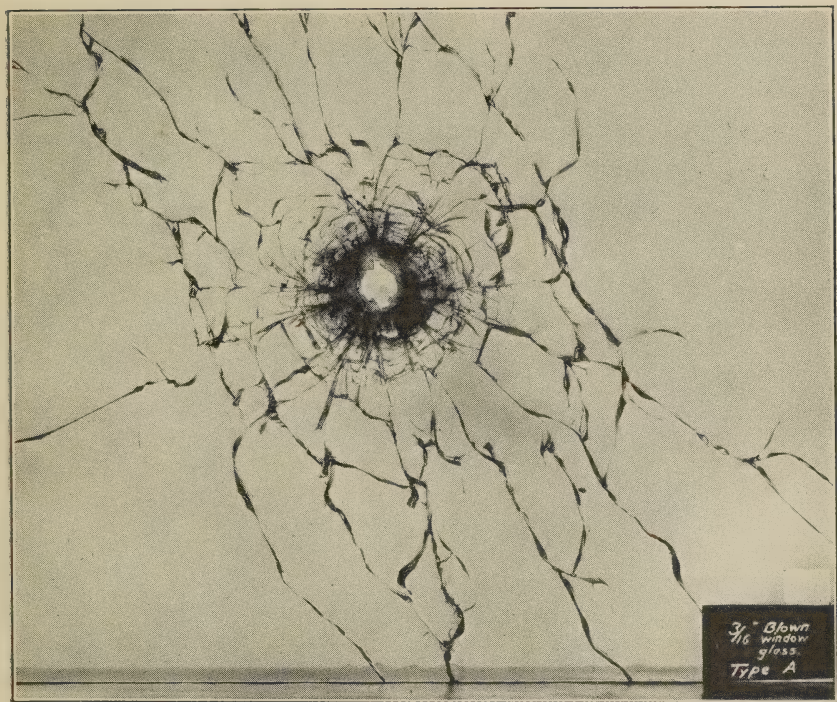


FIG. 2.

7. In handling and cleaning the samples, the celluloid was easily scratched or marred if there was any grit on the surface.

The effects of bullets fired perpendicular to the surfaces and against the uncoated sides of the Type A samples are shown in Figs. 1 to 4. These are typical fractures.

Impact Tests.

The samples used in this test were of the same size and kinds as those used in the firing tests, except that no $\frac{3}{16}$ " plate glass was tested. The specimens were placed in the frame used in the firing tests and this was supported solidly on the steel frame of an impact testing machine of the pendulum type. The pendulum

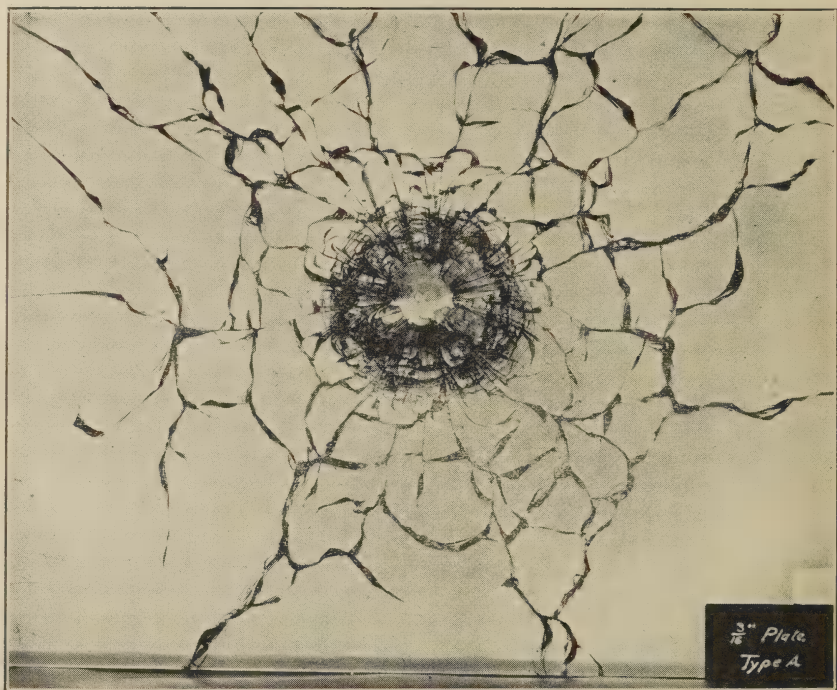


FIG. 3.

consisted of a $1\frac{1}{4}$ pound flattened steel ball at the end of a 24" stiff wire arm. The hammer had a spherical striking surface with a radius of $1\frac{1}{8}$ ".

In making these tests the pendulum was first allowed to swing through 5° , then 10° , and so on, the angle of swing being increased each time by 5° until fracture occurred. However, a

fall through 90° was not sufficient to break some of the specimens, in which cases the hammer was dropped repeatedly through 90° until the piece was fractured. The angle or the number of repetitions at 90° was recorded. On several of the samples of protective glass the test was continued until there was complete fracture of both glass and celluloid.



FIG. 4.

The energy of impact in foot pounds of a swinging pendulum, when impact occurs as in this case perpendicularly below the point of suspension, is calculated by the use of the following formula:

$$E = 1 - \cos \text{angle } A \times L \times W,$$

in which

Angle A = angle with vertical made by the pendulum arm at the time of release.

L = length of arm in feet.

W = weight of hammer in pounds.

It is impossible to figure the effect of repetitions of the same blow or blows of increasing severity—due to lack of data on the mechanical properties of glass. If the time required to alter the apparatus had been available, the energy of impact necessary to fracture the strongest samples could have been determined by using a heavier hammer or a longer pendulum arm.

TABLE 1.
Results of impact tests.¹

Nominal thickness of glass. Inches.	Description.	Average angle at fracture. Degrees.	Average energy at fracture. Ft. lbs.
1/8	Plain	42.5	0.66
1/8	Treated side exposed	50.0	0.89
1/8	Glass side exposed	45.0	0.73
3/16	Plain	90.0 ²	2.46
3/16	Treated side exposed	65.0	1.44
3/16	Glass side exposed	90.0 ³	2.46
1/4	Plain	62.5	1.35
1/4	Treated side exposed	70.0	1.64
1/4	Glass side exposed	82.5	2.17

The chief results of these tests are shown in Table 1. The following observations were made at the time of testing:

1. The plain glass was broken into many small pieces. The treated samples cracked but the pieces were held together by the celluloid coating. Only a few small splinters were loosened immediately under the hammer.

2. After the first fracture occurred in the treated samples, only two or three more blows were required to break the celluloid and splinter the glass.

3. The cracked area was smaller on the thinner samples.

4. Fewer but more extended cracks were caused when the blow fell on the treated side than on the glass side.

¹ Each of the values given in the table is the average of two tests.

² One sample did not break with 170 repetitions at 90°.

³ Repeated an average of 8 times. Energy of impact figured simply as of 90°.

Attention may be called to the fact, as shown in Table 1, that the $\frac{3}{16}$ " uncoated blown window glass was stronger than the $\frac{1}{4}$ " plate glass. Also, that the amount of energy required to cause the first crack in the glass was not materially increased by the celluloid coating.

Cross Bend Tests.

The samples used were 2" by 12" and of three thicknesses, as in the preceding tests. The $\frac{1}{8}$ " and $\frac{1}{4}$ " thicknesses were plate glass and the $\frac{3}{16}$ " thickness was blown window glass.

In making the tests, two wooden bearing blocks of triangular section were placed on the platform of a small counter scales so as to give a span of 10 inches. A strip of glass was laid on these and the load applied to the middle of the sample by means of a rod screwed downward through a steel yoke placed above the scales. The lower end of the rod was provided with a bearing block of semi-circular cross-section resting in a ball and socket joint. Thin bearing strips of rubber were interposed between the glass and the three blocks.

TABLE 2.
Results of cross bend tests.¹

Nominal thickness. Inches.	Description.	Actual average thickness. Inches.	Average load at failure. Pounds.
$\frac{1}{8}$	Plain	0.142	20.5
$\frac{1}{8}$	Treated side up	0.145	17.5
$\frac{1}{8}$	Treated side down	0.152	31.5
$\frac{3}{16}$	Plain	0.175	36.0
$\frac{3}{16}$	Treated side up	0.186	25.0
$\frac{3}{16}$	Treated side down	0.190	46.5
$\frac{1}{4}$	Plain	0.229	44.5
$\frac{1}{4}$	Treated side up	0.241	38.5
$\frac{1}{4}$	Treated side down	0.242	60.0

The results of these tests are shown in Table 2. Fracture occurred under the point of application of the load and was generally in the form of a V-shaped group of cracks.

¹ Each of the values given in this table is the average of two tests.

A study of Table 2 shows that the treated samples of a given kind and thickness were about 15 per cent weaker than the plain glass when the celluloid side was in compression and about 40 per cent stronger when the celluloid side was in tension.

Summary.

The following recapitulation may be made of the salient points of these tests:

1. It is possible to determine some of the physical properties of sheet glass in a fairly accurate manner by the use of a comparatively simple testing apparatus.
2. In both the impact and cross bend tests, the blown window glass was stronger than the plate glass.
3. While the energy of impact necessary to produce fracture increased with the thickness of the plate glass, the amount of cracking occurring at the time of initial fracture also increased.
4. The force of the blow required to crack a piece of glass of a given kind and thickness was not materially increased by the celluloid coating, but the shattered glass remained in place while the plain glass was scattered.
5. In the cross bend tests the treated glass of a given kind and thickness was about 15 per cent weaker than the plain glass when the celluloid coated side was in compression and about 40 per cent stronger when the celluloid coated side was in tension.

ERRATA SLIP

"Some Phenomena in Glaze Reduction," by H. B. Henderson, Vol. 1, No. 3, page 148 *et seq.*

Page 149 line 4 from the top omit the word "somewhat."

Page 149 line 12 from the bottom change the word "graphitic" to "graphite."

Page 151 line 14 from the top omit the words "iron oxide."

Page 151 line 19 from the top insert the words "some of" after the word "glaze."

Page 152 line 12 from the top insert the word "ferrous" before the word "iron."

Page 152 change the footnote to read: "Sosman and Hostetter, *Trans. American Inst. Mining Engineers, Bull.* 126."

Page 153 line 4 from the top change "will" to "may."

Page 153 line 23 from the top change "color" to "coloring matter."

Page 155 lines 11 and 12 omit the clause "except by the assumption of transformation and diffusion effects."

Page 155 line 15 from the top change "but" to "and."

Page 155 line 17 from the top change "probable" to "evident."

Page 155 line 19 from the top insert the clause "if it is iron" after the word "iron."

American Ceramic Society

YEAR BOOK
1918

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- Foersterling, Hans, Ph.D., Jamesburg, New Jersey, Second Vice-President, Roessler and Hasslacher Chemical Company.
- Footitt, Frank F., Room 216, Ceramic Building, Urbana, Illinois, University of Illinois.
- Ford, G. Bergen, Caudler Bldg., Atlanta, Ga., B. Mifflin Hood Company.
- Forester, Herbert, Box 37, Cleveland, Ohio, Principal, Veritas Firing System Company.
- Forman, L. P., Arnold, Pa., American Window Glass Company.
- Forst, Arthur D., Trenton, New Jersey, President, Robertson Art Tile Company.
- Forst, D. Parry, 73 North Clinton Ave., Trenton, New Jersey, Robertson Art Tile Company.
- Fowler, William E., Paxtonville, Pa., Paxton Brick Company.
- Franzheim, C. Merts, Wheeling, West Virginia, The Charles M. Franzheim Company.
- Fraser, W. B., Dallas, Texas, President, Fraser Brick Company.
- Fraunfelter, Charles D., Zanesville, Ohio, President, Ohio Pottery Company.
- Freese, H. H., 446 South Union St., Galion, Ohio, Mechanical Engineer, E. M. Freese Company.
- Frerichs, Wm. D., 111 Broadway, New York City, Federal Terra Cotta Company.

- Frey, Frank A.**, Milwaukee, Wisconsin, Enameling Department, Geuder, Paeschke and Frey Company.
- Fridricksen, Christian**, Wheeling, West Virginia, Wheeling Tile Company.
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- Fuhrmann, F. J.** (Address unknown.)
- Fuller, Ralph L.**, 1119 Guardian Bldg., Cleveland, Ohio, Harshaw, Fuller and Goodwin Company.
- Fulper, William H.**, Flemington, New Jersey, Secretary-Treasurer, Fulper Pottery.
- Fulton, Kenneth I.**, Portland, Indiana, Honor Roll.
- Fulweiler, Walter H.**, 319 Arch St., Philadelphia, Pa., Chief Chemist, United Gas Improvement Company.
- Gahris Willard I.**, Sebring, Ohio, Limoges China Company.
- Galloway, Walter B.**, Philadelphia, Pa., President, Galloway Terra Cotta Company.
- Garrison, Amos**, 417 South First St. West, Salt Lake City, Utah.
- Gates, A. W.**, Colchester, Illinois, President and Treasurer, Gates Fire Clay Company.
- Gates, Major E.**, Terra Cotta, Illinois, Superintendent, American Terra Cotta and Ceramic Company.
- Gavin, Gordon P.**, Kalamazoo, Michigan, Superintendent, Kalamazoo Sanitary Manufacturing Company.
- Gaylord, George L.**, 14 Holland Ave., Westfield, Mass., General Manager, Vitriified Wheel Company.
- Gehrig, Edward F.**, Detroit, Michigan, Research Engineer, Detroit Stove Works.
- Geiger, Carl F.**, 7 Baltimore St., Dayton, Ohio, Chief Draughtsman and Engineer, The Manufacturers Equipment Company.
- Geiger, Charles F.**, Department of Ceramics, Rutgers College, New Brunswick, N. J.
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- Gerber, Albert C.**, Toledo, Ohio, Honor Roll.
- Gibbs, Arthur E.**, 1006 Widener Bldg., Philadelphia, Pa., Head of Research Department, Pennsylvania Salt Manufacturing Company.
- Giesey, V. A.**, 318 Citizens Bldg., Cleveland, Ohio, President, National Refractories Company.
- Gilbert, Frank W.**, Rochester, Pa., Pittsburgh Grinding Wheel Company.
- Gildard, Warren R.**, Ballston Lake, New York, Research Laboratory, General Electric Company, Schenectady, N. Y.
- Gillinder, James**, 11 Orange St., Port Jervis, New York, Superintendent, Gillinder Brothers.

- Gilmore, R. B.**, E. Liberty Branch, Y. M. C. A., Pittsburgh, Pa., Ceramic Engineer, Vesuvius Crucible Company.
- Gladding, Augustus L.**, Lincoln, California, Gladding, McBean and Company.
- Godfrey, Miss Lydia B.**, Grand View-on-Hudson, New York, Director, Glen Tor Ceramic Studio.
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- Good, Harry N.**, Pittsburgh, Pa., Ceramic Engineer, Pittsburgh Testing Laboratory.
- Gorton, Arthur F., Ph.D.**, Toledo, Ohio, Research Physicist, Buckeye Clay Pot Company.
- Grafton, Charles O.**, Muncie, Indiana, Treasurer and General Manager, Gill Clay Pot Company.
- Grainer, John S.**, Box 21, Spring Lake, Michigan, Challenge Refrigerator Company.
- Grampp, Otto**, 205 Farwell Ave., Milwaukee, Wis., Superintendent, A. J. Lindeman and Hoverson Company.
- Grant, DeForest**, 101 Park Ave., New York City, President, Federal Terra Cotta Company.
- Grant, W. Henry**, St. Marys, Pa., Elk Fire Brick Company.
- Green, J. L.**, St. Louis, Mo., President, Laclede-Christy Clay Products Company.
- Greene, R. W.**, Mayfield, Kentucky, Kentucky Construction and Improvement Company.
- Greener, George C.**, 198 Clarendon St., Boston, Mass., Director, North Bennett Street Industrial School.
- Greenwood, G. W.**, Uniontown, Pa., United Fire Brick Company.
- Gregori, John N.**, Chicago, Illinois, Kiln Burner, Northwestern Terra Cotta Company.
- Gregorius, Thomas K.**, Corning, New York, Ceramic Engineer, Corning Glass Works.
- Gregory, M. Creveling**, Corning, New York, Ceramic Engineer, Corning Brick, Terra Cotta and Tile Company.
- Gregory M. E.**, Corning, N. Y., Proprietor, Corning Brick, Terra Cotta and Tile Co.
- Grueby, William H.**, Boston, Mass, President and General Manager, Grueby Faience Company.
- Guastavino, Rafael, Jr.**, Fuller Bldg., Broadway and 23rd St., New York City, President, R. Guastavino Company.
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- Haeger, E. H.**, Dundee, Illinois, Haeger Brick and Tile Company.
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- Hall, Clarence A.**, 18 McPherson St., Mount Airy, Pa., Research Department, Pennsylvania Salt Manufacturing Company.
- Hall, Herman A.**, Nelsonville, Ohio, Pulverized Fire Clay Company.
- Hall, Robert T.**, East Liverpool, Ohio, Secretary and Treasurer, Hall China Company.
- Hall, William C.**, 1302—3rd National Bank Building, Atlanta, Georgia, Vice-President, Atlanta Terra Cotta Company.
- Hamilton, James**, Trenton, New Jersey, Superintendent, Ideal Pottery of The Trenton Potteries.
- Handke, Paul A.**, 260 S. Academy St., Galesburg, Illinois, Purington Paving Brick Company.
- Hanna, Harold H.**, Crystal City, Mo., Pittsburgh Plate Glass Company.
- Hansen, Abel**, Fords, New Jersey, Proprietor and Manager, Fords Porcelain Works.
- *Hansen, Harry M.**, Maplehurst, Metuchen, New Jersey.
- Harbeck, H. F.**, Grand Haven, Michigan, President, Challenge Refrigerator Company.
- Hardesty, B. D.**, Syracuse, New York, Iroquois China Company.
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- Hardy, Isaac E.**, Momence, Illinois, Superintendent, Tiffany Enameled Brick Company.
- Hare, Robert L.**, Mexico, Mo., A. P. Green Fire Brick Company.
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- Harper, John L.**, Niagara Falls, New York, Hydraulic Power Company.
- Harris, Charles T.**, 356 Leader Building, Cleveland, Ohio, Secretary, Hollow Building Tile Manufacturers' Association of America.
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- Hatton, Richard D.**, 1673 Railway Exchange Bldg., St. Louis, Mo., Vice-President and General Manager, Laclede-Christy Clay Products Company.
- Heilman, Karl J.**, Tiffin, Ohio, Proprietor, Tiffin Brick Company.
- Heistand, Elza F.**, Muncie, Indiana, Superintendent, Crucible Department, Gill Clay Pot Company.

* Died October 13, 1918.

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- Herbst, Abram W., Canaan, Conn., New England Slag Company.
- Herron, James H., 1364 West Third St., Cleveland, Ohio, Consulting Engineer.
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- Hibbins, Thomas A., Wellsville, Ohio, General Business and Sales Manager, The Stevenson Company.
- Hipp, Ralph T., Massillon, Ohio, Massillon Stone and Fire Brick Company.
- Hipp, William G., Massillon, Ohio, Secretary and General Manager, Massillon Stone and Fire Brick Company.
- Hitchins, R. E., Olive Hill, Kentucky, General Manager, General Refractories Company.
- Hoehn, F. J., Carlinville, Illinois, Honor Roll.
- Hoffman, George E., Trenton, New Jersey, Secretary, Monument Pottery Company.
- Holmes, Harold W., Detroit, Michigan, Honor Roll.
- Hood, B. Mifflin, Atlanta, Georgia, President, Mifflin Hood Brick Company.
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- Hornung, Martin R., Shenango Pottery Co., Newcastle, Pa.
- Horton, J. M., Sebring, Ohio, E. H. Sebring China Company.
- Hostetler, G. R., Sugar Creek, Ohio, Superintendent, Sugar Creek Clay Products Company.
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- Hull, Addis E., Jr., Crooksville, Ohio, Ceramic Engineer, A. E. Hull Pottery Company.
- Hung, Shen, 52 Woodruff Ave., Columbus, Ohio.
- Hunt, F. Sumner, Chillicothe, Ohio, Honor Roll.
- Ireland, Harley R., Brazil, Indiana, Assistant Secretary and Treasurer, Hydraulic Press Brick Company.
- Irwin, Dewitt, East Liverpool, Ohio, Secretary, Potters' Supply Company.
- Ittner, Warren W., 327 N. Illinois St., Belleville, Illinois, The Malinite Company.
- Jackson, H. W., DuBois, Pa., General Manager, Jackson China Company.
- Jacobs, W. M., Charleroi, Pa., Pittsburgh, Plate Glass Company.
- Jacquart, Charles E., South River, New Jersey, Honor Roll.

- Jeffery, Joseph A., Detroit, Michigan, President, Jeffery-Dewitt Company.
- Jensen, A. Lawrence, 142-156 Green St., Brooklyn, New York, Empire China Works.
- Jensen, Charles H., 142-156 Green St., Brooklyn, New York, President, Empire China Works.
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- Justice, Ithamar M., Dayton, Ohio, Vice-President, Manufacturers' Equipment Company.
- Kalbfleisch, G. C., Tiffin, Ohio, Manager, Standard Manufacturing Company.
- Kanengeiser, Fred R., Poland, Ohio.
- Katzenstein, Leon, Worcester, Mass., Special Investigator, Norton Company.
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- Kempf, John R., Detroit, Michigan, Star Corundum Wheel Company.
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- Kent, G. G., Detroit, Michigan, Honor Roll.
- Keplinger, Robert B., Canton, Ohio, Assistant General Superintendent, Metropolitan Paving Brick Company.
- Kerr, W. B., Syracuse, New York, President, Iroquois China Company.
- Keuffel, Carl W., Adams and Third Sts., Hoboken, New Jersey, Keuffel and Esser Company.
- Kier, Samuel M., 2243 Oliver Bldg., Pittsburgh, Pa., President, Kier Fire Brick Company.
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- King, B. F., Colchester, Illinois, Manager, Brick and Tile Company.
- King, Earl O., Box 190, Baltimore, Maryland, American Refractories Company.

- Kleymeyer, H. C.**, Office 8, Furniture Bldg., Evansville, Indiana, General Manager, Standard Brick Manufacturing Company.
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- Knapp, Ernest W.**, Y. M. C. A., Canton, Ohio.
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- Koch, A. L.**, Minneapolis, Minn., Honor Roll.
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- Kraus, Louis P., Jr.**, 66—87th St., Brooklyn, New York, Research Engineer, Babcock and Wilcox Company.
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- Krieg, William G.**, 1515 Lumber Exchange Building, Chicago, Illinois.
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- Kurtz, John C.**, Rochester, New York, Bausch and Lomb Optical Company.
- Kurtz, Thomas N.**, Claysburg, Pa., Standard Refractories Company.
- Lacy, Miss Mattie Lee**, Denton, Texas, College of Industrial Arts.
- Laird, J. S.**, Ann Arbor, Michigan, Assistant Professor, Chemical Laboratory, University of Michigan.
- Lambie, J. M.**, Washington, Pa., Vice-President and Assistant General Manager, Findlay Clay Pot Company.
- Lamont, R. A., Jr.**, Salem, Ohio, General Manager, National Sanitary Company.
- Landers, William F.**, Indianapolis, Indiana, Superintendent, U. S. Encaustic Tile Works.
- Lardin, R. H.**, Creighton, Pa., Assistant Chemist, Pittsburgh Plate Glass Company.
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- Larkins, Samuel B.**, Salineville, Ohio, Superintendent National China Company.
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- Linder, Cyril S., Creighton, Pa., Pittsburgh Plate Glass Company.
- Lindley, Jacob, Tiltonville, Ohio, Riverside Potteries Company.
- Livingston, H. J., Buffalo, New York, National Grinding Wheel Company.
- Lloyd, Harry, Irondale, Ohio, Colonial Clay and Coal Company.
- Locke, F. M., Victor, New York, Manufacturer of Porcelain Insulators.
- Loeffler, R. W., Frankfort, Indiana, Superintendent, Ingram-Richardson Manufacturing Company.
- Long, George E., Jersey City, New Jersey, Vice-President Joseph Dixon Crucible Company.
- Longenecker, H. L., Cambridge, Maryland, Manager, Cambridge Brick Company.
- Lord, F. G., Lewiston, Pa., Sales Manager, Pennsylvania Pulverizing Company.
- Louthan, William B., East Liverpool, Ohio, Manager, Louthan Supply Company.
- Lovatt, John, 1308 Brunswick Bldg., Trenton, New Jersey, Kiln Builder.
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- Luke, Charles H., New Bethlehem, Pa., Climax Fire Brick Company.
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- Maddison, E. A. (Address unknown.)
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- Maddock, Henry E., Trenton, New Jersey, John Maddock and Sons.
- Maddock, John, Trenton, New Jersey, John Maddock and Sons.
- Maicas, Oscar R., 1200 Hudson St., Hoboken, New Jersey, Sales Engineer, Didier-March Company.
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- Malkin, William R., East Liverpool, Ohio, Salesman, B. F. Drakenfeld & Company, Inc.

- Malm, Arthur T.**, 18 Orne St., Worcester, Mass., Factory Investigator, Research Laboratories, Norton Company.
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- Maltby, Alfred**, Corning, New York, Superintendent, Brick Terra Cotta and Tile Company.
- Mandle, I.**, 1318 Wright Bldg., St. Louis, Mo., Secretary and Treasurer, The Mandle Clay Mining Company.
- Mandle, Sidney**, 1318 Wright Bldg., St. Louis, Mo., Assistant Treasurer, Mandle Clay Mining Company.
- *Mandler, C. J.**, Toledo, Ohio, President, Allen Filter Company.
- Manion, L. W.**, 1370 Greenfield Ave., S. W., Canton, Ohio, Designer and Builder of Industrial Furnaces.
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- Marks, Melville**, 29 Broadway, New York City, Moore and Munger.
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- Martin, S. C.**, Kittanning, Pa., Kittanning Brick and Fire Clay Company.
- Martz, Joseph A.**, Honor Roll.
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- Miller, R. W., Lt.**, Indianapolis, Indiana, Honor Roll.
- Milligan, Frank W.**, Parkersburg, West Virginia, Manager, General Porcelain Company.
- Mills, H. F.**, Noblesville, Indiana.
- Millsom, Walter C.**, Macomb, Illinois.
- Miner, Harlan S.**, Gloucester City, New Jersey, Chief Chemist, Welsbach Company.

* Died December 1918.

- Minor, Frederick K.**, Oliver Building, Pittsburgh, Pa., Sales Engineer, Celite Products Company.
- Moncrieff, James W.**, Grand Rapids, Michigan, Honor Roll.
- Moore, Earl J.**, Greenville, Ohio, Honor Roll.
- Moore, H. W.**, Perth Amboy, New Jersey, Chief Chemist, Atlantic Terra Cotta Company.
- Moorshead, T. C.**, Alton, Illinois, Chief Engineer, Illinois Glass Company.
- Morgan, Fred A.**, Honor Roll.
- Morris, Paul R.**, 300 East 9th Ave., Tarentum, Pa., Chemist, Pittsburgh Plate Glass Company.
- Morrow, Robert P.**, 1513 Rockefeller Bldg., Cleveland, Ohio, Salesman, Harbison-Walker Refractories Company.
- Morton, John M.**, Zanesville, Ohio, Superintendent, Mosaic Tile Company.
- Moses, James**, Trenton, New Jersey, Mercer Pottery Company.
- Mossman, P. B.**, 315 Union Arcade Bldg., Pittsburgh, Pa.
- Motz, W. H.**, Akron, Ohio, Secretary and Treasurer, Colonial Sign and Insulator Company.
- Moulding, J. M.**, Momence, Illinois, Tiffany Enameled Brick Company.
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- Mueller, Theodore E.**, Louisville, Kentucky, Manager, Louisville Works, Standard Sanitary Manufacturing Company.
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- Murray, G. A.**, Honor Roll.
- Myers, Charles H.**, 498½ Poplar St., Murray, Utah, Superintendent, Utah Fire Clay Company.
- Myers, Scott P.**, Uhrichsville, Ohio, Superintendent, Robinson Clay Products Company.
- McAllister, James E.**, Trenton, New Jersey, J. L. Mott Company.
- McBean, Atholl**, 311-317 Crocker Bldg., San Francisco, California, Secretary, Gladding McBean and Company.
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- McCoy, William**, 334 Adair Ave., Zanesville, Ohio, Mechanical Engineer, American Encaustic Tiling Company.

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- McDougal, Taine G.**, Flint, Michigan, Champion Ignition Company.
- McDowell, J. S.**, Pittsburgh, Pa., Research Department, Harbison-Walker Company.
- McDowell, S. J.**, Flint, Michigan, Ceramic Engineer, Champion Ignition Company.
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- McGregor, John R.**, 208 S. La Salle St., Chicago, Illinois, Eagle-Picher Lead Company.
- McHose, Malcolm M.**, Perth Amboy, New Jersey, Manager, L. H. McHose, Inc.
- McKaig, W. Wallace**, Cumberland, Maryland, McKaig Machinery Foundry and Supply Works.
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- MacMichael, P. S.**, Auburn, Washington, President, Northern Clay Company.
- McMillan, Herbert S.**, Detroit, Michigan, Manager and Secretary, Porcelain Enameling and Manufacturing Company.
- McNaughton, Malcolm**, Jersey City, New Jersey, Superintendent, Joseph Dixon Crucible Company.
- McPadden, J. H.**, 26 Cortlandt St., New York City, Secretary Quigley Furnace Specialties Company.
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“In Memoriam”

Shanks, John A. G. (Killed in Action)

Yates, Alfred

Walduck, Charles L.

Mandler, C. J.

Hansen, Harry (Died in Service)

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The Saxon China Company, Sebring, Ohio.
The Sebring Pottery Company, Sebring, Ohio.
Smith-Phillips China Company, East Liverpool, Ohio.
Standard Pottery Company, East Liverpool, Ohio.
Star Porcelain Company, Trenton, New Jersey.
Steubenville Pottery Company, Steubenville, Ohio.
Streator Clay Manufacturing Company, Streator, Illinois.
The Taylor, Smith and Taylor Company, Chester, West Virginia.
R. Thomas and Sons Company, East Liverpool, Ohio.
C. C. Thompson Pottery Company, East Liverpool, Ohio.
The Trenle China Company, East Liverpool, Ohio.
Veritas Firing System, Prospect Laboratories, Trenton, New Jersey.
Vitro Manufacturing Company, Bessemer Bldg., Pittsburgh, Pa.
Vodrey Pottery Company, East Liverpool, Ohio.
Warwick China Company, Wheeling, West Virginia.
The West End Pottery Company, East Liverpool, Ohio.

MEMBERSHIP.

The preceding lists have been brought up-to-date, January 1, 1919. Owing to the well organized and executed campaign on the part of the Committee on Membership for new members, the enrollment of the Society has undergone an unusual and highly gratifying growth. This has been in spite of the disturbed conditions prevailing abroad and augurs well for the future welfare and prosperity of the Society.

The following analysis is interesting:

MEMBERSHIP, FEBRUARY 1, 1917.

Honorary members.....	4
Active members, resident.....	71
Active members, foreign.....	5
Associate members, resident.....	414
Associate members, foreign.....	43
<hr/>	
TOTAL.....	537

MEMBERSHIP, FEBRUARY 1, 1918.

Honorary members.....	4
Life members.....	1
Active members, resident.....	79
Active members, foreign.....	9
Associate members, resident.....	568
Associate members, foreign.....	56
Contributing members.....	33
<hr/>	
TOTAL.....	750

MEMBERSHIP, JANUARY 1, 1919.

Honorary members.....	3
Life members.....	1
Active members, resident.....	99
Active members, foreign.....	6
Associate members, resident.....	722
Associate members, foreign.....	72
Contributing members.....	73
<hr/>	
TOTAL.....	976

HONOR ROLL—MEMBERS.

Allen, F. B.	Hornung, M. R.
Anderson, Robert E.	Horsley, Thomas N.
Arnold, Howard C.	Howat, Walter L.
Ayer, Kenneth R.	Hunt, F. Sumner
Bacon, R. F.	Jacquart, Charles E.
Balmert, Richard M.	Kent, G. G.
Bartells, H. H.	Koch, A. L.
Bates, Charles E.	Martz, Joseph A.
Best, Harold A.	Miller, R. L.
Brockbank, Clarence J.	Moncrieff, James W.
Broga, Wilson C.	Moore, Earl J.
Brown, Wilbur F.	Moore, Joseph K.
Bucher, L. R.	Morgan, Fred A.
Byers, Louis L.	Murray, G. A.
Carter, Benjamin F.	McCann, James S.
Chase, John A.	Orton, Edward, Jr.
Chormann, O. I.	Primley, Walter S.
Clayter, Frederic C.	Ramsden, C. E.
Cowan, R. Guy	Rathjeins, G. W.
Crew, H. F.	Rixford, Guy L.
Dorst, Max	Robertson, H. S.
Ferguson, Richard D.	Schaulin, George M.
Ferguson, Robert F.	Springe, Otto
Fisher, G. P.	Sproat, Ira E.
Fulton, Kenneth I.	Steinhoff, F. L.
Geiger, Chas. F.	Thomas, Charles W.
Gerber, Albert C.	Tilton, C. B.
*Hansen, Harry	Van Schoick, E. H.
Helser, Perry D.	Walker, Francis W., Jr.
Hoehn, F. J.	Walker, Prescott H.
Holmes, Harold W.	Whitford, Wm. G.
Hope, Herford	Yowell, J. B.
Horning, Roy A.	

* Died in service.

HONOR ROLL—STUDENT BRANCHES.

New York State Student Branch.

Ayars, Lister	King, Walter
Blumenthal, George	Lobaugh, Frank E.
Crawford, George	Negus, Wayland
Hagar, Donald	Reid, W. Harold
Harrington, Henry W.	Sheppard, Mark
Kane, Donald	Sherwood, Robert F.
Kenyon, Spicer	

Ohio State University Student Branch.

Blum, J. W.	Mauck, F. J.
Callahan, H. D.	Merritt, L. M.
Cramer, W. E.	Minor, J. A.
Davis, H. E.	Minton, G. Z.
Dodd, C. M.	Ramsay, John
Foster, H. D.	Robinson, H. A.
Gregorius, J. S.	Shaw, A. E.
Gunther, F. W.	Sieverling, P. A.
Hall, Rex	Skinner, E.
Hartford, F. M.	Stephens, W. H.
Jones, R. E.	Stowe, G. T.
Kirschner, C. F.	Vance, E. D.
Koos, E. K.	Watkins, R. T.
Lintz, E. H.	Zwerner, C. G.

University of Illinois Student Branch.

Baker, Earl B.	Hummeland, Ralph W.
Bates, Charles E.	Kennelley, Griffith S.
Byers, Louis L.	Kling, Carl L.
Carter, Benjamin F.	Leibson, Jacob S.
Chittenden, Robert M.	Moncrieff, James W.
Christopher, Arthur B.	Sortwell, Harold H.
Davis, Raymond E.	Twells, Robert
Golden, Dios E.	Zalaski, John T.
Greenbaum, Charles S.	

RULES OF THE SOCIETY.

[Revised 1918.]

I.

OBJECTS.

The objects of the American Ceramic Society are to develop the ceramic arts and the sciences related to the silicate industries by means of meetings for the reading and discussion of papers, the publication of scientific literature, and other activities.

II.

MEMBERSHIP.

The Society shall consist of Honorary Members, Active Members, Associate Members, Affiliated Members, and Contributing Members.

Honorary Members must be persons of acknowledged professional eminence whom the Society wishes to honor in recognition of their achievements in ceramic science or art. Their number shall at no time exceed two per cent of the combined active and associate membership.

Active Members must be persons competent to fill responsible positions in ceramics. Only Associate Members shall be eligible to election as Active Members and such election shall occur only in recognition of attainments or of services in the science, technology, or art, of the silicate industries.

Associate Members must be persons interested in the silicate or allied industries.

Contributing Members must be persons, firms, or corporations, who, being interested in the Society, make such financial contributions for its support as are prescribed in Section III.

Honorary Members shall be nominated for election by at least five Active Members and approved by the Board of Trustees. Their nomination shall be placed before the Society at an annual meeting and to be elected they must receive the affirmative vote of at least ninety per cent of those voting, by letter ballot, at the next succeeding annual meeting.

To be promoted to active membership Associate Members must be nominated in writing by an Active Member, seconded by not less than two other Active Members, and approved by the Board of Trustees. Their nomination must be accompanied by a statement of their qualifications and to be elected they must receive an affirmative vote of the majority of the members of the Board of Trustees.

A candidate for associate membership must make application upon a form provided by the Board of Trustees, which shall contain a written statement

of the age and professional experience of the candidate and a pledge to conform to the laws, rules, and requirements of the Society. Such application must be endorsed by two Active Members of the Society as sponsors and must be approved by the Board of Trustees. The Board may act by letter ballot upon such application at any time, after which and upon payment of the fees and dues prescribed in Section III, an approved candidate may be enrolled on the appropriate list of the Society.

Affiliated Members are those members of a Local Section who are not otherwise connected with the Society. Their rights and privileges relate solely to the affairs of the Local Sections to which they belong.

Contributing Members may be enrolled on the appropriate list of the Society at any time upon the payment of the dues prescribed in Section III.

All Honorary Members, Active Members, Associate Members, and Contributing Members shall be equally entitled to the privileges of membership, except that only Active Members shall be entitled to vote and hold office. The roster of each of these grades of membership shall be printed separately in at least one publication issued by the Society annually. Any person may be expelled from any grade of the membership of the Society if charges signed by five or more Active Members be filed against him and if a majority of the Board of Trustees examine into said charges and sustain them. Such person, however, shall first be notified of the charges against him and be given a reasonable time to appear before the Board of Trustees or to present a written defense, before final action is taken.

III.

DUES.

Honorary Members shall be exempt from all fees or dues.

The initiation fee of Active Members shall be ten dollars and if this be not paid within three months after the date of election, the latter shall be null and void. The annual dues shall be fixed by the Board of Trustees and shall not exceed ten dollars, four dollars of which shall be a subscription to the *Journal of the American Ceramic Society*.

The initiation fee of Associate Members shall be five dollars, payable within three months after date of election. The annual dues shall be fixed by the Board of Trustees but shall not exceed five dollars, four dollars of which shall be a subscription to the *Journal of the American Ceramic Society*.

Affiliated Members are liable only for the dues and assessments of the Local Sections.

Contributing Members shall pay no initiation fee. The annual dues shall be fixed by the Board of Trustees, but shall not be less than twenty-five dollars, four dollars of which shall be a subscription to the *Journal of the American Ceramic Society*. The privileges of membership shall begin upon payment of the annual dues.

Any Active or Associate Member in arrears for over one year may be suspended from membership by the Board of Trustees until such arrears are

paid and in event of continued dereliction, may be dropped from the rolls. Active Members in arrears are not eligible to vote. The annual dues of Active and Associate Members are payable within three months succeeding the date of the annual meeting.

IV.

OFFICERS.

The affairs of the Society shall be managed by a Board of Trustees, consisting of a President, Vice-President, Honorary Secretary, Secretary, Treasurer, and five Trustees. The officers, other than the Honorary Secretary and three Trustees, shall be elected from the Active Members at the annual meeting and shall hold office until their successors are elected and installed. The retiring President shall serve as Trustee for two years.

The President, Vice-President, Secretary, and Treasurer shall be elected for one year and the Trustees for three years; and no President, Vice-President, or Trustee shall be eligible for immediate re-election to the same office.

The Board of Trustees may from time to time, within their discretion, elect any past Secretary of the Society as Honorary Secretary to perform such duties as they may designate.

The President shall have general supervision of the affairs of the Society under the direction of the Board of Trustees and shall perform such other duties as pertain to his office.

The Secretary shall be, under the direction of the President and Board of Trustees, the executive officer of the Society. He will be expected to attend all meetings of the Society and of the Board of Trustees, prepare the business therefor and duly record the proceedings thereof.

He shall see that all moneys due the Society are carefully collected and without loss transferred to the custody of the Treasurer. He shall carefully scrutinize all expenditures and use his best endeavor to secure economy in the administration of the Society. He shall personally certify the accuracy of all bills or vouchers on which money is to be paid and shall countersign the checks drawn by the Treasurer against the funds of the Society when such drafts are known by him to be proper and duly authorized by the Board of Trustees. He shall have charge of the books of account of the Society and shall furnish monthly to the Board of Trustees a statement of monthly balances. He shall present annually to the Board of Trustees a balance sheet of his books as of the 31st of January and shall furnish from time to time such other statements as may be required of him.

He shall conduct the correspondence of the Society and keep full records of the same. He shall transmit promptly to the Board of Trustees for their consideration all communications not of routine nature. He shall report promptly to all Active Members the results of all balloting on the business of the Society unless otherwise ordered by the Board of Trustees. He shall perform all other duties which may from time to time be assigned to him by the Board of Trustees.

The Secretary may be paid a salary to be determined by the Board of Trustees.

The Secretary shall furnish a suitable bond for the satisfactory performance of his duties.

The Treasurer shall receive all money and deposit the same in the name of the Society. He shall invest all funds, not needed for current disbursements, as shall be ordered by the Board of Trustees. He shall pay all bills when certified and audited as provided by these Rules or as ordered by the Board of Trustees. He shall make an annual report and such other reports as may be prescribed by the Board of Trustees. He shall furnish a satisfactory bond for the proper performance of his duties.

A vacancy in any office shall be filled by appointment by the Board of Trustees but the new incumbent shall not thereby be rendered ineligible for re-election to the same office at the next annual meeting. On the failure of any officer or any member of a committee to execute his duties within a reasonable time, the Board of Trustees, after duly warning such person, may declare the office vacant and appoint a new incumbent.

A majority of the Board of Trustees shall constitute a quorum, but the Board of Trustees shall be permitted to carry on such business as they may desire by letter.

V.

ELECTIONS.

At the annual meeting a Nominating Committee of five Active Members, not officers of the Society, shall be appointed.

At least sixty days before the annual meeting this committee shall send the names of the nominees to the Secretary, who will immediately send a copy of the same to each Active Member. Any five Active Members may act as a self-constituted Nominating Committee and present the names of any nominees to the Secretary, provided this is done at least thirty days before the annual meeting. The names of all nominees, provided their assent has been obtained, shall be placed on the ballot without distinction as to nomination by the regular or self-constituted Nominating Committee, and shall be mailed to each Active Member, not in arrears, at least twenty days before the annual meeting. The voting shall be confined to the names appearing on this ballot. The ballot shall be enclosed in an inner blank envelope and the outer envelope shall be endorsed by the voter and mailed to the Secretary. The blank envelope shall be opened by three scrutineers appointed by the President, who will report the result of the election at the last session of the annual meeting. A plurality of affirmative votes cast shall elect.

VI.

MEETINGS.

The annual meeting shall take place on the first Monday in February, or as soon thereafter as can be arranged, at such place as the Board of Trustees

may decide, at which time reports shall be made by the Board of Trustees, Treasurer, and scrutineers of election, and the accounts of the Treasurer shall be audited by a committee of three appointed by the President. Ten active members shall constitute a quorum at any regular meeting and a majority shall rule unless otherwise specified.

The order of business at the annual meeting shall be:

1. President's address.
2. Reading of minutes of last meeting.
3. Reports of the Board of Trustees and Treasurer.
4. Old business.
5. New business.
6. Reading of papers.
7. Announcement of election of officers, Honorary and Active Members.
8. Installation of officers and new members.
9. Appointment of committees.
10. Adjournment.

Other meetings may be held at such times and places during the year as the Board of Trustees may decide, but at least twenty days' notice shall be given of any meeting.

The President shall appoint at the annual meeting a committee of five, to be known as the Summer Meeting Committee, whose duty it shall be to arrange for a summer excursion meeting at some suitable point. The expenses of the Summer Meeting Committee in arranging the program of visits and for printing, rooms, and facilities for meetings shall be borne by the Society.

VII.

STANDING COMMITTEES.

The following Standing Committees shall be appointed annually by the Board of Trustees:

1. Rules.
2. Publications.
3. Membership.
4. Standards.
5. Local and Student Sections.
6. Papers and Programs.
7. Coöperation.
8. War Service.

The Committee on Rules shall consist of five members. It shall receive all recommendations relating to changes of Rules and shall report upon the same to the Secretary for transmission to the Society. It shall have power to propose changes in the Rules of the Society.

The Committee on Publications shall consist of the Editor and four members. The duties of the Editor and Committee on Publications are defined under Article XI on Publications.

The Committee on Membership shall consist of at least five members and shall have the power to appoint sub-committees. Its function shall be to undertake systematically the enlargement of the membership of the Society amongst those interested in the silicate and allied industries.

The Committee on Standards shall consist of at least five members and shall have the power to appoint sub-committees. It shall submit written reports, resolutions, and recommendations, relating to tests of materials and products. The Committee may report at any regular meeting of the Society. For adoption, these reports, resolutions, and recommendations must be submitted in printed form to the members of the Society at least six months before a vote may be taken, during which time any amendments, changes, or corrections suggested by any member may with the approval of the Committee be incorporated in the report, resolution, or recommendation. The reports, resolutions, and recommendations as amended shall then be submitted by letter ballot to the Active Members. A two-thirds vote shall be required for adoption.

The Committee on Local and Student Sections shall consist of five members. Its duties shall be to promote the organization and welfare of Local and Student Sections.

The Committee on Papers and Programs shall consist of the Chairmen of the various Divisions, the Secretary of the Society, and such other persons as the Board of Trustees may deem advisable. Its duties shall be to procure papers and discussions for the meetings and publications of the Society. The Committee may require an abstract of any paper submitted before placing it upon a program.

The Committee on Coöperation shall consist of at least five members. Its duties shall be to promote the interests of the Society by coöperation with other societies and organizations and to secure recognition of the Society by any proper means.

The Committee on War Service shall consist of at least five members. Its duties shall be to investigate National problems pertaining to the silicate industries and to stimulate research and production.

VIII.

DIVISIONS.

Professional groups to be known as Divisions of the Society and to be organized from members of the Society may be authorized by the Board of Trustees for stimulating the growth and development of the Society, when such action shall seem wise and expedient. Any member of the Society may register in any Divisions of the Society in which he is interested.

The officers of a Division shall be a Chairman and a Recording Secretary. Officers of Divisions shall be elected annually by ballot at the last session

of the Division held during the annual meeting of the Society and shall take office at the close of the meeting at which they were elected. They shall hold office for one year or until their successors are elected. The Board of Trustees shall fill any vacancies occurring through death or resignation among the officers of a Division.

A Division shall have the right to make by-laws for its own government, which shall be subject to the approval of the Board of Trustees and must not be inconsistent with the Rules of the Society, and a committee to draw up such by-laws shall be appointed at the first meeting held by the Division.

Any Division may raise or collect funds to be expended for its own purposes and may have the entire management and control of said funds, in so far as said management and control does not conflict with any provisions of the Rules or with the Charter of the Society.

Any Division may be dissolved by the Board of Trustees for good and sufficient reasons.

IX.

LOCAL SECTIONS.

Local Sections, each carrying some distinguishing title prefixed to the words "Section of the American Ceramic Society," may be authorized by the Society.

The purposes of such sections shall be to strengthen and extend the work of the Society as defined in Section I of its Rules by more frequent meetings in local centers than are possible to the Society as a whole and by bringing the benefits of the work to persons who would not otherwise be reached.

Application for permission to form a Local Section must be in writing and signed by not less than ten members of the Society in good standing, residing in the general locality where the Section is to be formed, of whom one at least shall be an Active Member. To be considered at any given meeting an application must be filed with the Secretary at least thirty days prior to the date of the meeting and notice that the application is pending must appear in the program of the meeting. To be granted the application must receive the affirmative vote of two-thirds of those present. In event of affirmative action the Society will issue a charter to the applicants authorizing them to form a Section under the name proposed. Charters for Local Sections may be temporarily suspended by the Board of Trustees for cause, but no charter can be permanently rescinded except by vote of two-thirds of those present at a regular meeting of the Society, after due publication in the program of the meeting that the matter is pending.

Local Sections shall have power to make their own rules and by-laws except that they shall not pass any rule or by-law which is in conflict with the Rules of the Society.

The officers of Local Sections shall be a Chairman, a Secretary, a Councilor, and such others as the Section may prescribe. The duties of the Chairman and Secretary shall be such as usually pertain to those offices. The

Councilor shall be an Active Member of the Society. He shall be elected by the Local Section and it shall be his duty to advise the Section in all matters pertaining to its relations with the Society and to make an annual report to the Society regarding the work and status of the Section. The names of the Chairman, Secretary, and Councilor of each Section shall appear in the roster of the Society.

Any person interested in the silicate and allied industries is eligible to membership in a Local Section.

Local Sections shall have power to fix their own dues or assessments, such dues or assessments being in addition to and independent of the regular dues and assessments of the Society upon its members. No Section shall have authority to incur debt in the name of the Society or for which the Society may become liable.

X.

STUDENT BRANCHES.

Student Branches, each carrying some distinguishing title prefixed to the words "Student Branch of the American Ceramic Society," may be established in institutions in which regular courses of instruction in ceramics are maintained.

The purposes of such Student Branches shall be to strengthen and extend the work of the Society, as defined in Section I of the Rules, by enlisting the interest and support of students in ceramics while still in school and by stimulating the spirit of ceramic research among them.

Application to form a Student Branch in any institution must be in writing, signed by not less than five regularly enrolled students in good standing and endorsed by two or more members of the Society. The application must be filed and acted upon as provided for Local Sections in Section IX, and may be suspended or revoked for cause in the same manner.

Student Branches shall have power to make their own rules and by-laws, except that they shall not pass any rule or by-law in conflict with the Rules of the Society.

The officers of Student Branches shall be a Chairman, a Secretary, a Councilor, and such others as the Student Branch may prescribe. The Chairman and Secretary shall be elected by the Student Branch and their duties shall be such as usually pertain to those offices. The Councilor shall be an Active Member of the Society, appointed by the Board of Trustees to act in this capacity to the Student Branch. The duties of the Councilor shall be to advise the Student Branch in all matters pertaining to its relations to the Society and to make an annual report to the Society regarding the work and status of the Student Branch. The names of the Chairman, Secretary, and Councilor for each Student Branch shall appear in the roster of the Society.

Membership in a Student Branch shall be limited to the instructional force and regularly enrolled students of schools in which branches are located,

subject to the rules of the school concerned governing outside activities of students.

Student Branches shall have power to fix their own dues and assessments and, as such, shall pay no dues or initiation fees to the Society. No Student Branch shall have authority to incur debt in the name of the Society or for which the Society may become liable.

Members of a Student Branch as such shall pay no dues or initiation fees to the Society but upon depositing a certificate of good standing from their Secretary, may purchase from the Society its publications at the same rate as Associate Members of the Society. This privilege shall cease when the student's connection with the school ceases, but members of a Student Branch, upon leaving school, may at once become Associate Members of the Society by depositing their certificates, making proper application, and paying the regular initiation fee.

XI.

PUBLICATIONS.

The Board of Trustees may employ, at a suitable compensation, an editor of the publications of the Society.

The Committee on Publications shall have general supervision of the publications of the Society and of contracts and expenditures connected therewith, subject to the approval of the Board of Trustees.

In the consideration of papers offered for presentation or publication those papers containing matter readily found elsewhere, those specially advocating personal interests, those carelessly prepared or controverting established facts, and those purely speculative or foreign to the purposes of the Society, shall be rejected. The Committee on Publications shall determine which papers shall be printed. The Committee may return a paper to the writer for correction and emendation and may call to its aid one or more members of special experience relating to the subject treated, either to advise on the paper or to discuss it.

The Committee on Publications shall provide for the publication of a monthly periodical entitled the *Journal of the American Ceramic Society*, the subscription price of which shall be four dollars to members and six dollars to non-members.

One copy of the paper-bound edition of the *Journal* shall be sent prepaid to each member of the Society not in arrears. No member shall be furnished with more than one copy for any single year in return for his regular subscription. A member shall be permitted to complete by purchase one file of the publications of the Society at less than the current commercial rate, the amount to be fixed by the Board of Trustees and to be called the member's rate.

The Secretary shall have the custody of all publications of the Society, shall keep them safely stored and insured, and shall sell them to the public at prices which shall be fixed by the Board of Trustees. The Board of Trus-

tees shall also, from time to time, fix the price of the volumes remaining unsold and shall have authority to refuse to sell the back volumes of the Transactions and Journals except in complete sets, at such time as the quantity remaining of any number becomes so small as in their judgment to warrant such action.

The Editor shall request the author of each article appearing in the Journal of the Society to fill out and sign, within a definite time limit, a form, specifying the number of reprints of said article, if any, which he desires. This form shall contain a table from which can be computed the approximate cost at which any reprints will be furnished. In event that the expense of furnishing the desired number of reprints is large, the Board of Trustees may require the author to pay part or all of the cost involved before the publication of the reprints is begun. On receipt of such signed order within the time limit set the Editor shall cause to have printed the desired number of copies. If the author makes no reply or replies after the time limit has expired then the Society will not be responsible for the publication of any reprints of the article in question except at the usual market price for the printing of new matter.

No one shall have the right to demand the publication of an article independent of the discussion which accompanied it and no one having taken part in a discussion upon an article shall be entitled to order reprints of the discussion separately and apart from the article itself.

The Society is not, as a body, responsible for the statement of facts or opinions expressed by individuals in its publications.

XII.

PARLIAMENTARY STANDARD.

Roberts' "Rules of Order" shall be the parliamentary standard on all points not covered by these rules.

XIII.

AMENDMENTS.

To amend these Rules the amendment must be presented in writing at a regular meeting of the Society and, if approved by the Committee on Rules or by any ten Active Members, must be printed on a ballot and sent out not earlier than thirty nor later than sixty days after the adjournment of the meeting at which the amendment was presented. If the said letter ballot shows an affirmative vote of not less than two-thirds of the total vote cast within fourteen days of the date of mailing, then the same shall be declared carried and shall at once become effective.

PUBLICATIONS.

TRANSACTIONS, AMERICAN CERAMIC SOCIETY.

			Bound in cloth.
Vol. I.	1899,	110 pages.....	\$4 75
Vol. II.	1900,	278 pages.....	4 75
Vol. III.	1901,	238 pages.....	4 75
Vol. IV.	1902,	300 pages.....	4 75
Vol. V.	1903,	420 pages.....	5 75
Vol. VI.	1904,	278 pages.....	4 75
Vol. VII.	1905,	454 pages.....	4 75
Vol. VIII.	1906,	411 pages.....	4 75
Vol. IX.	1907,	808 pages.....	5 75
Vol. X.	1908,	582 pages.....	5 75
Vol. XI.	1909,	632 pages.....	6 25
Vol. XII.	1910,	882 pages.....	6 25
Vol. XIII.	1911,	837 pages.....	6 25
Vol. XIV.	1912,	888 pages.....	6 25
Vol. XV.	1913,	747 pages.....	6 25
Vol. XVI.	1914,	611 pages.....	6 25
Vol. XVII.	1915,	815 pages.....	6 25
Vol. XVIII.	1916,	947 pages.....	6 25
Vol. XIX.	1917,	707 pages.....	6 25

Complete set..... \$106 75

To members of the Society a reduction of 40 per cent will be made from the above prices. Members cannot purchase more than one copy of each volume at members' rate.

NOTE—Vols. II, V, IX, X, XII and XIX will not be sold except in complete sets.

The Society has also published the following books, which will be sold net, at the prices listed, to the public and members alike:

- The Collected Writings of Dr. Hermann August Seger, Volume I,
Contains (a) Treatises of General Scientific Nature. (b) Essays
relating to Brick and Terra Cotta, Earthenware and Stoneware,
and Refractory Wares. 552 pages. Bound in cloth..... \$7 50
- The Collected Writings of Dr. Hermann August Seger, Volume II.
(a) Essays on White Ware and Porcelain. (b) Travels, Letters
and Polemics. (c) Uncompleted works and extracts from the
archives of the Royal Factory. 605 pages. Bound in cloth.... 7 50
- A Bibliography of Clays and the Ceramic Arts, by Dr. John C. Branner,
1906. 451 pages. Bound in cloth. Contains 6027 titles
of works on Ceramic subjects..... 2 00
- A Directory of Dealers in Raw Ceramic Materials, 60 pages..... 50

The above publications can be obtained of the Secretary and will be shipped at the consignee's expense by express or parcels post to any address on receipt of the price. To all who purchase a complete set of the Transactions, a copy of the Branner Bibliography is given free. All checks or money orders are payable to The American Ceramic Society.

CHAS. F. BINNS, *Secretary.*

Alfred, N. Y.

ANNUAL REPORT OF THE BOARD OF TRUSTEES.

TO THE MEMBERS OF THE AMERICAN CERAMIC SOCIETY:

The Board of Trustees has prepared the following statement of the business and condition of the Society for the period February 1, 1917 to February 1, 1918:

RECEIPTS.

Brought forward February 1, 1917.....		\$1,489.12
Dues.....	\$3,642.88	
Fees.....	861.85	
Contributing Members.....	500.00	
Transactions.....	2,179.00	
Branner's Bibliography.....	13.20	
Seger's Collected Writings.....	75.00	
Reprints.....	115.63	
Convention Visitors.....	19.00	
Error in Deposit of Oct. 26, 1917.....	2.00	
Total Receipts for year ending January 31, 1918.....	\$7,408.56	7,408.56
Total.....		\$8,897.68

DISBURSEMENTS.

Publication of Vol. XIX:		
Stenographic report.....	\$	154.00
Telegrams.....		4.02
Drawings, Illustrations and Engravings.....		487.74
Ptg., Binding, Casing and Typing.....	1,464.93	
Editor's salary.....	600.00	
		2,710.69
Reprints of Vol. XVII and XVIII.....		246.75
Transportation of volumes.....		186.73
Balance due on Volume XVIII.....		105.59
Convention expenses.....		239.80
Seger's Collected Writings and Binding.....		75.15
Binding early volumes.....		110.65

AMERICAN CERAMIC SOCIETY.

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Association Dues (Nat'l Fire Prot. Ass'n).....	30.00	
Membership Committee.....	227.46	
Traveling expenses (arranging Summer meeting)....	35.00	
Nat'l Exposition Chemical Industry.....	44.50	
Refund.....	3.75	
Insurance and storage on volumes.....	88.75	
Salary Ass't Secretary.....	300.00	
Extra clerk hire.....	577.25	
Postage, Stationery, Supplies, etc.....	762.99	
Telegrams.....	7.82	
Typewriter Rental.....	40.00	
Exchange charges.....	1.00	
		<hr/>
Total Disbursements for year.....		\$5,793.88
		<hr/>
Balance Jan. 31, 1918.....		\$3,013.80

REPORTS OF COMMITTEES AND STUDENT BRANCHES, 1918 MEETING.

REPORT OF THE COMMITTEE ON MILITARY AND ECONOMIC PREPAREDNESS.

This committee was created at the New York meeting and Prof. Edward Orton, Jr., was appointed chairman. Fortunately, he was able to remain with the work long enough to organize it before we lost him to the Army. The scope of the work comprised activities dealing, first, with direct war requirements, and second, those referring to economic matters affected by the war. The field was divided into sections according to the products most concerned with war needs. At the initial meeting the following sub-committees were organized:

Abrasives, R. C. Purdy, *Chairman*.

Chemical Porcelain, Charles F. Binns, *Chairman*.

Chemical Stoneware, R. H. Minton, *Chairman*.

Enameled Iron, R. D. Landrum, *Chairman*.

Electrical Porcelain, L. E. Barringer, *Chairman*.

Optical Glass, C. H. Kerr, *Chairman*.

Raw Materials, A. S. Watts, *Chairman*.

Refractories, A. V. Bleininger, *Chairman*.

The work of these committees for the year 1917-18 may be briefly summarized as follows:

Abrasives.—This committee, principally through its chairman, began its activity without delay by securing concerted action on the part of the manufacturers of grinding wheels. From among them a traffic committee was at once organized whose duty it was to move goods through embargoes so that each company could stock its yards with raw material. This was accomplished. Another committee was appointed to simplify the specifications for wheels which brought them to the question of machines and especially the size of arbors. It was necessary to specify the

arbor size in order that the Government could secure as many machines of one type as possible. There are also several other parts of machines that control the specifications of wheels and these have been considered by several committees. The Grinding Wheel Manufacturers' Association also has a War Service Committee, one member of which is in Washington all of the time. All of the work has been done by this organization but by men who are also members of the American Ceramic Society. The work has been completed and the final reports submitted.

Chemical Porcelain.—The principal needs of this work consisted in securing adequate specifications which would insure the production of good porcelain which would meet the requirements of the users. This has been done by the chairman who has devoted much time and attention to this subject. In a number of instances the specifications have been used to select ware for Government use.

Chemical Stoneware.—The work of this committee consisted to a large part in bringing about an organization of manufacturers for the purpose of securing a sufficient supply of clay, fuel and wood for forms, through the rigid embargoes. This involved a great deal of work on the part of Mr. Minton and his associates. They also looked after the prompt shipment of goods to the chemical plants which, in spite of the urgent need, was sometimes very difficult to accomplish, especially in the congested districts of the East. It was necessary to keep in touch with the War Industries Board, the various traffic committees, as well as the military authorities concerned. Some work has also been done towards the standardization of chemical stoneware.

Enameled Iron.—The work of this committee was of a somewhat diverse character. Assistance was rendered the Signal Corps to secure sheet metal parts through the use of the punch presses operated by manufacturers of enameled iron. The committee was able also to help the Government in securing the desired quantity and quality of enameled steel cooking utensils. Just now the Committee is working upon a standard specification for cooking utensils and hospital supplies for the Army and Navy.

This committee was instrumental also in having the manufacturers of sheet steel ware form a War Service Committee.

Electrical Porcelain.—This committee compiled a list of the porcelain articles needed by the Government but its attention was centered upon the spark plug problem, especially with reference to aeroplane engines. The several members of this committee, the laboratory of the General Electric Company and the Bureau of Standards worked along these lines, with reference to the spark plug itself, the cementing of the electrode and the assembling of the parts. Considerable work has been done along these lines and a general improvement has resulted from these efforts. The use of porcelains of a much higher maturing temperature, lower feldspar content and more constant thermal expansion has been brought about. Such problems are not restricted to the spark plug but apply to magnetos as well. In coöperation with the English a satisfactory insulation for magnetos has been worked out which is being manufactured in England today.

Optical Glass.—This committee was in touch with the developments in the production of this important material as well as with its most efficient use in optical instruments due to the connections of the chairman. The committee supplied technical information, abstracts, etc., to those interested and rendered such service as was within its province.

Raw Materials.—There has been a distinct lack of information concerning the sources of American raw materials used in the ceramic industries, a condition particularly trying during the stress of war time. Frequently, owing to embargoes or freight tie-ups, it has been found necessary to make changes in materials and for this purpose complete lists of miners and dealers were urgently needed. This need has been supplied by the committee, principally through the hard work of its chairman, by the publication of a Directory giving the names and addresses of 545 dealers in ceramic materials. This publication is still undergoing revision and will be reprinted from time to time.

Refractories.—This committee associated itself with the Refractories Manufacturers' Association and it was found desirable to organize a joint committee consisting of representatives of the principal government departments and manufacturers. This organization succeeded in interesting such men as Admiral Dyson, Commander Penn and other government officials in its work. Several meetings were held in Washington and the standard shapes adopted by the Refractories Manufacturers' Association were submitted for general acceptance by all the government departments. Work was begun on an extensive series of tests for the purpose of arriving at specifications covering the quality of refractories. This study was completed and the results issued by the Refractories Manufacturers' Association for distribution among its members. A great deal of work also had to be done with reference to clays for glass pots, graphite crucibles, special refractories such as magnesia spinel, and questions constantly brought up by different government departments. In coöperation with the Navy a study was made of light weight refractories for torpedo boats, destroyers and cruisers.

A. V. BLEININGER, *Chairman*.

February 11, 1918.

REPORT OF COMMITTEE ON SUMMER MEETING.

The members of this committee began early to canvass for the most favorable itinerary for a summer meeting. We took into consideration the fact that our people were interested most largely in the war and its issues as well as the character of the itinerary.

We met in Hornell, N. Y., Sunday afternoon and Monday morning of July 8 and 9, 1917. Those who met with Prof. Binns and Prof. Shaw on Sunday afternoon had a very delightful social time. On Monday, July 9th, 32 members and delegates went by motor bus from Hornell to Alfred. Here the day was spent most pleasantly with the faculty of the New York State School of Ceramics at Alfred University. The hearty welcome and cordial entertainment given by the Alfred faculty was most enjoyable. Much was learned by the visitors in the opportunity

to see in detail the most complete equipment and facilities for the teaching of Ceramics and for the making of ceramic researches. There probably is no laboratory more thoroughly equipped and more thoroughly organized than the laboratories of this school.

Late Monday afternoon the party motored back to Hornell and by train went to Corning where we spent a most delightful evening with Messrs. M. E. Gregory, F. R. Garder, Alfred Maltby and Dr. E. C. Sullivan.

Tuesday was devoted to visits to the plants of the Corning Brick, Terra Cotta & Tile Co., Corning Glass Works and the Stuben Glass Co. The members had the rare privilege of seeing in detail the manufacture of the now famous Pyrex Glass and had described and illustrated to them the manufacture of art glassware. The members had a rare opportunity in these visits to the Corning and Stuben Glass works and were very enthusiastic in their expression of appreciation.

Tuesday afternoon the Corning members entertained the visitors at a delightful dinner at the Corning City Club.

Wednesday morning the delegation which had now been increased in numbers took an early train from Corning to Watkins Glen, where they viewed one of the most picturesque wonders of Nature in America. Pictures and words would fail to convey an adequate description of the Glen. All who saw it made pledges to themselves for an early return visit.

After a delightful stay in and about the Glen and the Park the members took a noon train to Canandaigua where Clarence C. Keehan, Secretary and Assistant Manager of the Liske Mfg. Co., met the party, guided them to a restaurant where lunch had been arranged, and then through the large manufacturing plants.

The party arrived in Rochester, N. Y., late Wednesday afternoon. In the evening the party sought its own entertainment but it was mostly spent in exchange of greetings with the Rochester hosts and those who joined the party at this time. Thursday was spent in visiting the enameling plant of the Pfaudler Co., Taylor Instrument Co., and the Pennsylvania Feldspar Plant. The delegates were delightfully entertained at luncheon as guests

of these companies, and later at the beautiful park on Lake Ontario.

The party disbanded Friday evening after having enjoyed a week that was replete in things of Ceramic interest and opportunities, of seeing ceramic work which to most was not only novel but unknown, and seeing some of the most wonderful things that Nature has builded, with companionship that has already blossomed into lasting friendship on the part of many and, most, important of all, with a better understanding of the accomplishments and purposes of this Society, not only in general, but also as it relates to the individual members.

The official roster shows that nearly 60 members of the Society availed themselves of the opportunity of this meeting at one time or another and that there was at any time a minimum attendance of 32.

R. C. PURDY, *Chairman.*

February 12, 1918.

REPORT OF UNIVERSITY OF ILLINOIS STUDENT BRANCH.

The activities of the Student Branch have been somewhat curtailed during the past year owing to the generally prevailing conditions. A number of the members left school to enter military service before the end of the year. A further portion entered the Service during the summer, leaving only a small nucleus of members who returned to take up the work of the Society this year. The active membership has thus been reduced to fifteen.

The disorganization general in student bodies and the unsettled state of mind that most of the boys were in has further contributed to the difficulty of carrying out a well-planned program for the activities of the present year. Under these adverse conditions the members who have carried on the work this year have done exceedingly well. The following papers and lectures have been given at the several meetings:

"Plant Experiences," by J. W. Moncrieff and H. H. Sortwell.

"Firing Kilns with Forced Draft," by B. F. Carter.

"Electric Furnaces," by F. F. Footitt.

"Glass Notes," by J. E. Seabright.

"The Manufacture of Architectural Terra Cotta," An illustrated lecture, by Professor C. W. Parmelee.

"Research Notes," by Professors E. W. Washburn, C. W. Parmelee and R. K. Hursh.

"The Manufacture of Abrasives," an illustrated lecture, by Mr. Hermann A. Plusch, Abrasive Co., Phila., Pa.

One of the meetings during the year was made an "Open House" evening at the Ceramics building, when friends of the members and others who were interested were shown the laboratories and saw something of the work. This was especially planned for the benefit of the freshmen who had thus far had no opportunity to learn the character of the work ahead of them.

The Student Branch obtained and presented to the Department of Ceramic Engineering a large framed portrait of Professor Charles Wesley Rolfe who was so largely instrumental in obtaining the establishment of the Department at the University.

The present officers of the Branch at Illinois are: President; James W. Moncrieff; Vice-President, Griffith S. Kennelley; Secretary-Treasurer, Benjamin F. Carter.

R. K. HURSH, Councilor.

February 12, 1918.

REPORT OF THE IOWA STATE COLLEGE STUDENT BRANCH.

The number of students in ceramic engineering at Iowa State College has decreased very much on account of the War. Of the small enrollment we had last year, there are now eight men actually in the Army, three of these being in France. Several of the men enrolled had been drafted and expected to be called to the colors at an early date.

Nevertheless, the men remaining have held regular meetings every two weeks of the school year and have shown considerable enthusiasm in the work of the Student Branch. The arrangement and presentation of the programs has been entirely in the hands of the students, the faculty taking no hand in these. The

young men have shown originality and initiative in this work and a wide variety of subjects, most of them relating to practical questions in ceramic engineering, have been discussed.

Mr. E. Raddewig is Chairman and Mr. F. A. Ohlsan is Secretary of the Student Branch.

HOMER F. STALEY, Councilor.

February 12, 1918.

REPORT OF THE NEW YORK STATE STUDENT BRANCH.

The Society was greatly interested at the opening of the year in reports given by some of the members who had spent the Summer in practical work. Two successive meetings were arranged at which these reports were presented and discussed. It was felt to be very desirable that students would find opportunity during their college course to spend one or more summers in this way.

At the meeting of November 14, Prof. J. B. Shaw gave a talk on the production and use of enamels for steel and iron. The comprehensive and practical view given of this part of the ceramic field was new to many of the members and a great deal of interest was aroused.

About this time the Student Branch was somewhat disorganized and temporarily depressed by the loss of its chairman. This young man, a senior, had been carrying a heavy burden at home in the sickness and ultimate death of his father. Being thus compelled to postpone his graduation for a year he left college and went to work in the industry. After a short period of readjustment a new chairman was elected and the work was resumed. An interesting meeting resulted from a desire to hear what the lower classmen could do. A member of the Sophomore class was placed in charge and a program was successfully carried through.

Following upon this a session was devoted to hearing theses problems discussed by the senior class and finally an evening was assigned to a consideration of the preparation and use of the different types of cement.

Reviewing the year as a whole the result of the work has been satisfactory but not ideal. The dislocation alluded to, though

temporary, was serious because the school year is too short to admit of effective readjustments. Each year, however, provides a small supply of experience which will gradually accumulate into a fund.

CHAS. F. BINNS, Councilor.

February 12, 1918.

REPORT OF OHIO STATE UNIVERSITY STUDENT BRANCH.

The past year has been very satisfactory considering the fact that about fifteen of our students have enlisted, leaving only about thirty-five men in the course. We have, however, maintained our organization and held the following interesting meetings:

October 23, 1917. Meeting for organization and election of the following officers: E. D. Vance, *Chairman*; C. M. Dodd, *Vice-Chairman*; and J. W. Hepplewhite, *Secretary-Treasurer*. The object and purposes of the Society were explained by Professor Watts.

November 20, 1917. Address by R. T. Stull, U. S. Bureau of Mines, on "Paving Brick."

January 15, 1918. Address by Mr. H. G. Schurecht, U. S. Bureau of Mines, on "The Manufacture of Glass Pots."

The financial statement of the Branch shows \$37.24 on hand, \$48.00 collected, and \$84.04 expended by order of the Branch, leaving a cash balance of \$1.20.

ARTHUR S. WATTS, Councilor.

February 12, 1918.

IN RETROSPECT.

The first volume of the Journal of the American Ceramic Society is completed with this number.

Appointed in February 1918, the Committee on Publications was authorized to publish a monthly Journal to take the place of the annual volume of Transactions. The Committee took up the work promptly but several months were required to decide upon the many questions involved, such as the proper title and form of the magazine, actual size, subject matter to be included, advertising, publishing contracts, copyright, etc., etc. It

was decided to issue the entire twelve numbers for 1918 even though several months of the year had already elapsed and after the necessary preliminary arrangements the January number or Volume I, No. 1, appeared in July, 1918.

With but six months in which to issue twelve numbers, considerable exertion was necessary upon the part of the Editor, the Publishers and all concerned and many seemingly unavoidable delays were encountered. The volume has been completed in time, however, to permit of Volume II starting sufficiently early in 1919 to ensure its appearance at approximately equal monthly intervals and completion by January 1920.

Bearing in mind the broad field of industrial operations covered by the ceramic industries and the need of the Journal's readers for a well-diversified list of professional papers, the Committee on Publications has endeavored to secure meritorious papers in all fields and the following tabulation will indicate the degree of success attained:

Subject.	No. of Papers.
Clays—Occurrence and Uses.....	5
Methods of Testing (raw materials and finished products, physical and chemical).....	10
Drying and Driers.....	3
Kilns.....	5
Glass.....	9
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Enamels for cast iron and sheet steel.....	7
Pottery and porcelain.....	7
Terra Cotta.....	4
Cements, lime and plaster.....	5

Certainly a wide field is covered in this list and there is much of interest and value to all interested or engaged in ceramic work.

Perhaps some important fields were not sufficiently represented but this is due entirely to not having contributions from capable men in such branches. For Volume II the Committee on Publications is in a position to promise even a greater degree of diversification, while still maintaining and even advancing the degree of technical excellence.

The Committee on Publications desires to thank all who have contributed to the success of Volume I, the authors of the various papers published, the pioneer advertisers who accepted the value of the advertising medium upon faith, and the members of the American Ceramic Society who have offered helpful suggestions and coöperation.

We are encouraged by Volume I; we hope it has proven both pleasing and profitable to its readers and we will endeavor to serve you as well or better in Volume II.

COMMITTEE ON PUBLICATIONS.

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